

PB-236 765

ATMOSPHERIC PHOTOCHEMICAL SMOG  
MEASUREMENTS OVER SAN FRANCISCO BAY

L. A. Cavanagh, et al

Stanford Research Institute

Prepared for:

Coordinating Research Council, Incorporated  
California State Air Resources Board  
Environmental Protection Agency

August 1973

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| <b>BIBLIOGRAPHIC DATA SHEET</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                           | 1. Report No.<br>CRC-APRAC-CAPA-12-72-1 | 2.                                                  | PB 236 765 |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| 4. Title and Subtitle<br>Atmospheric Photochemical Smog Measurements Over San Francisco Bay — Vol. I—                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                           |                                         | 5. Report Date<br>August 1973                       |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| 7. Author(s)<br>L. A. Cavanagh and J. H. Smith                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                           |                                         | 8. Performing Organization Rept. No.<br>SRI 2092    |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| 9. Performing Organization Name and Address<br>Stanford Research Institute<br>Menlo Park, California 94025                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                           |                                         | 10. Project/Task/Work Unit No.<br>CRC-APRAC CAPA-12 |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                           |                                         | 11. Contract/Grant No.                              |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| 12. Sponsoring Organization Name and Address<br>Coordinating Research Council, Inc. 30 Rockefeller Plaza, New York, N.Y.; Environmental Protection Agency, Research Triangle Park, N.C. and Air Resources Board, 1025 P St. Sacramento, Cal.                                                                                                                                                                                                                                                                                                                                                                                                                                            |                           |                                         | 13. Type of Report & Period Covered<br>Final        |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| 15. Supplementary Notes<br>Not releasable to the public until October 1974.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                           |                                         | 14.                                                 |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
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| Air Pollution                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Air Mass                  |                                         |                                                     |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| Pollutants                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Hydrocarbons              |                                         |                                                     |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| Aerosol                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Ozone                     |                                         |                                                     |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| Particulates                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | Nitrogen Oxides           |                                         |                                                     |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| Photochemical                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Aldehydes                 |                                         |                                                     |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| Aerometric                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Peroxyacyl Nitrates (PAN) |                                         |                                                     |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| Carbon Monoxide                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                           |                                         |                                                     |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| Air Parcel                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                           |                                         |                                                     |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| 17b. Identifiers: Open-Ended Terms<br>San Francisco Bay, California                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                           |                                         |                                                     |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
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| 17c. COSATI Field/Group 13B; 14B; 07E. ;                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                           |                                         |                                                     |            |                           |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
| 18. Availability Statement<br>Releasable to the General Public.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                           |                                         | 19. Security Class (This Report)<br>UNCLASSIFIED    |            | 21. No. of Pages<br>125   |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                           |                                         | 20. Security Class (This Page)<br>UNCLASSIFIED      |            | 22. Price<br>\$15.25-2.25 |               |          |            |              |         |       |              |                 |               |           |            |                           |                 |  |            |  |



STANFORD RESEARCH INSTITUTE  
Menlo Park, California 94025 · U.S.A.

*Final Report*

*August 1973*

## ATMOSPHERIC PHOTOCHEMICAL SMOG MEASUREMENTS OVER SAN FRANCISCO BAY

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*Prepared for:*

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ENVIRONMENTAL PROTECTION AGENCY  
DIVISION OF METEOROLOGY  
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711  
CRC APRAC CONTRACT CAPA-12-72 and EPA CONTRACT 68-02-1009

AIR RESOURCES BOARD  
1025 P STREET  
SACRAMENTO, CALIFORNIA 95814  
CONTRACT 2-021

SRI Projects 2092 and 2098

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## ABSTRACT

In a research program to measure composition and concentration of smog constituents in a moving air parcel, SRI outfitted a houseboat for use as a mobile laboratory and used a helicopter as an airborne laboratory. From these laboratories a research team made measurements over San Francisco Bay in the autumn of 1972.

Four sampling days were analyzed extensively, and the observed measurements were correlated. A data tape containing all of the air quality measurements is available. The data from the four selected days were analyzed to determine the correlation of the ratio  $\frac{[\text{NO}][\text{O}_3]}{[\text{NO}_2]}$  to solar intensity and NO concentrations. The correlation to solar intensity was low (correlation coefficient = -0.09), and the correlation to NO concentrations was high (correlation coefficient = 0.87). The concentrations of NO over the Bay appear to be inhomogeneously distributed. The NO concentration varied by factors as high as 6 (from 6 to 40 pphm) over distances of 5 kilometers or less.

Operational techniques and the appropriate logistics were developed to effectively coordinate the surface and airborne mobile laboratories. The study substantiated that a mobile laboratory can follow marked air parcels if meteorological conditions are favorable. Virtually no photochemical activity was present during the experimental program. However, the measurement data obtained could provide useful data for simulation modeling at concentration levels equivalent to air quality standards.

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# GLOSSARY

|                 |                                                  |
|-----------------|--------------------------------------------------|
| APC             | aerosol particle counter                         |
| ARB             | California Air Resources Board                   |
| BAAPCD          | Bay Area Air Pollution Control District          |
| BB              | San Francisco Bay Bridge                         |
| CN              | condensation nuclei                              |
| CRC             | Coordinating Research Council                    |
| DDi             | distilled deionized                              |
| EPA             | Environmental Protection Agency                  |
| ESCA            | Electron Scattering Cross-Section Analysis       |
| FID             | flame ionization detector                        |
| GC              | gas chromatograph                                |
| GC-MS           | gas chromatograph-mass spectrometer              |
| HC              | total hydrocarbon, excluding methane             |
| HP              | Hunter's Point                                   |
| NDIR            | nondispersive infrared                           |
| NO <sub>x</sub> | the sum of NO and NO <sub>2</sub> concentrations |
| OP              | Oyster Point                                     |
| PAN             | peroxyacyl nitrate                               |
| ppb             | parts per billion                                |
| pphm            | parts per hundred million                        |
| ppm             | parts per million                                |
| ppm C           | parts per million carbon, as hexane              |
| PVC             | polyvinyl chloride                               |
| SF              | San Francisco                                    |
| SLH             | San Leandro Harbor                               |
| THC             | total hydrocarbon                                |

#### ACKNOWLEDGMENTS

The authors of this report gratefully acknowledge the significant contributions of many people, including the other members of the houseboat crew: Mr. Louis Salas, Mr. Albert H. Smith, and Ms. Joyce Kealoha. Mr. Irwin Sauer was the instrument operator on board the helicopter. The analysis phase could not have been completed without the assistance of Mr. F. L. Ludwig. Laboratory support was ably provided by Mr. August Pijma.

## I INTRODUCTION

Photochemical smog results from photochemical reactions in the atmosphere that occur when nitrogen oxides and hydrocarbons are present. The reaction products include ozone, peroxyacyl nitrates (PAN), aldehydes, and a variety of secondary reaction products. To date, knowledge of the photochemical smog reaction process is largely based on controlled experiments in laboratory test chambers (smog chambers) and on statistical correlation analyses using atmospheric data on photochemical smog. In the latter case, most of the data have come from observations in the Los Angeles Basin.

As yet not satisfactorily resolved in the smog-forming process is the question of the importance of specific types of hydrocarbons, i.e., the olefins and other highly reactive types as compared to the less reactive aromatics. Another question is the significance of the ratio of nitrogen oxides to hydrocarbons in the photochemical mixture. Chamber experiments are now being used to judge the significance of hydrocarbon reactivity and hydrocarbon to  $\text{NO}_x$  ratios in order to postulate smog formation mechanisms. Ultimately, such studies could serve as a basis for revised air pollution control regulations and air quality standards on photochemical smog constituents such as  $\text{NO}_2$ , hydrocarbons, and oxidant or ozone. Chamber studies cannot simulate all the variabilities of the real atmosphere, and thus increased efforts have been made to carry out detailed aerometric analyses in Los Angeles. The basic goal is a realistic simulation model of photochemical smog.

The interpretation of aerometric measurements from Los Angeles, however, presents major problems. One of the more important is the great complexity of the area sources and their emissions. For example, any

sampling station in Los Angeles will be surrounded by sources of both hydrocarbons and  $\text{NO}_x$  at distances varying from the street just outside the door to the freeway 20 miles away. As a result, each sample will contain a wide mixture of emissions that have had various histories, times for reaction, and exposures to atmospheric influences. Although partial evaluations of the Los Angeles aerometric data have been published, the analyses leave unanswered many questions about the real photochemical smog system because of the difficulties in interpretation.

Knowledge of photochemical processes gained through laboratory and aerometric studies is frequently applied to the development or improvement of photochemical simulation models. Progress in improved simulation models is limited to a great extent by the lack of suitable aerometric data to evaluate these models. Photochemical models that are recognized to provide a realistic simulation of photochemical processes include those developed by Eschenroeder,<sup>1</sup> Seinfeld,<sup>2</sup> and Wayne.<sup>3</sup> The model developed by McCracken is currently used for prediction of carbon monoxide concentrations.<sup>4</sup> However, the McCracken model will be extended to include reactive pollutants and applied to the San Francisco Bay Area. Aerometric data, primarily from the Los Angeles Basin, have been used to evaluate the above photochemical models.

A research program was undertaken by SRI employing a concept unique to aerometric surveys, where both surface and airborne measurements were made in a marked, moving air parcel. The measurements were made over San Francisco Bay where changes in composition and concentration of pollutants occur without significant addition of fresh reactants. The primary objective of the program was to obtain aerometric data in a different locality, and to relate the changes in composition and concentration in an aging air mass to time and meteorological factors. The acquired data are presented in a format

suitable for evaluation of recognized photochemical models.

A secondary objective was to evaluate the methodology and techniques required to study smog constituents in a marked, moving air parcel. In addition to the study of gaseous pollutants funded by the Coordinating Research Council and the Environmental Protection Agency, a complementary research program funded by the California Air Resources Board was undertaken concurrently to demonstrate the feasibility of studying the aerosol constituents of photochemical smog from a mobile laboratory on the Bay. The data from these two research projects were to be coordinated and shared. Therefore, this final report incorporates data from both projects and is submitted to all organizations supporting this research.

## II SUMMARY

The primary objective of the research program undertaken by SRI was to measure the changes in composition and concentration of pollutants in a marked, moving air parcel. The photochemical reactions that occur in a single air mass were studied in a Lagrangian mode by a unique measurement approach. A houseboat was outfitted as a mobile air quality laboratory to measure smog constituents over San Francisco Bay. A helicopter was outfitted with instrumentation and used as an airborne laboratory to measure pollutant gradients, both horizontal and vertical. The air parcel to be measured was marked by a free-floating constant level balloon (a tetroon). The changes that occurred in the pollutant concentrations were related to time and meteorological factors.

The measurement phase of the research program was undertaken during the autumn of 1972. Unfortunately, the normal meteorological conditions conducive to smog formation did not develop. The autumn of 1972 was the "cleanest" year during the 10-year period that measurements have been made by the Bay Area Air Pollution Control District. Although, photochemical activity was uniformly low throughout the measurement period, pollutant concentration data were obtained on 15 days; of these, four sampling days have been analyzed in detail. These analyses address meteorological factors, pollutant concentrations, pollutant concentration gradients, particulate compositions, and particulate size distributions where appropriate. The four days selected for analysis were 21 September, 25 October, 26 October, and 2 November of 1972. On September 21, measurements were made following an air parcel from downwind of San Francisco for 2 hours down the axis of the Bay. Moderate photochemical activity

was observed during this sampling day. On October 25, an air parcel was tracked for 45 minutes near San Mateo Bridge; limited photochemical activity was observed. On October 26, an air parcel was tracked from San Francisco to Berkeley; little or no photochemical activity was observed. On 2 November, an air parcel was tracked for 2 hours from mid San Francisco Bay to a point south of the San Mateo Bridge; moderate photochemical activity was observed.

The conclusions reached on the basis of the experimental data indicate that the approach used is a viable technique for the study of photochemical smog processes. The methods and techniques that were developed for operating a houseboat mobile laboratory in conjunction with an airborne mobile laboratory were successful. The data obtained during the experimental program will be useful for modeling photochemical processes when pollutant concentrations approach the ambient air quality standards. The data will be of limited usefulness to verify models under conditions of moderate to heavy photochemical activity. The  $[\text{NO}][\text{O}_3]/[\text{NO}_2]^*$  ratio is discussed in detail on the basis of observed measurements of solar intensity and NO concentrations. On the basis of limited data analysis, a good correlation of the ratio with NO (correlation coefficient = 0.87) concentrations and a poor correlation with solar intensity was obtained (correlation coefficient = -0.09). Removal of data when the NO concentration was greater than 15 pphm (indicative of the injection of freshly polluted air to the air mass) did not improve the correlation with solar intensity.

The observed concentrations of NO over the Bay appear to be inhomogeneously distributed. The NO concentrations varied by factors

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\*Square brackets are used to indicate the concentration of a gas.

of as high as 6 (from 6 to 40 pphm) over distances of 5 kilometers or less. These inhomogeneities in NO concentrations were not accompanied by corresponding significant increases in the concentration of NO<sub>2</sub>, CO, or Aiken nuclei. The concentration of ozone, though present at low concentrations, does not decrease markedly in the areas where high concentration of NO are observed. Careful examination of the data, the mode of operation of the houseboat, and instrument functionality indicate that the observed measurements are valid. The cause or origin of these NO inhomogeneities cannot be identified on the basis of available meteorological data.

A data tape containing all the air quality measurements obtained by the houseboat mobile laboratory and a description of the tape format are provided as part of this final report.

### III THE 1972 SMOG SEASON

This research program was undertaken in anticipation of "normal" meteorological conditions in the San Francisco Bay Area. Usually, during the smog season the occurrence of low wind-speed conditions results in several intervals in which pronounced photochemical activity is observed. In 1971, a CRC-EPA funded study was undertaken to determine the feasibility of investigating the formation of photochemical smog in the San Francisco Bay Area. Although 1971 was considered the cleanest year of a decade by the San Francisco Bay Area Air Pollution Control District (BAAPCD), oxidant measurements made during 1971 by SRI, and analysis of BAAPCD oxidant measurements from 1967, indicated that a comprehensive research program undertaken during a normal year could produce valuable data about formation and scavenging of photochemical pollutants. It was emphasized in the report of the feasibility study that a comprehensive research program should be undertaken over a period of two years to ensure that the mobile laboratories could be operational over a sufficient number of sampling days in which appreciable photochemical activity was present. However, it was anticipated that even if 1972 was as clean as 1971, the objectives of the research program could be accomplished in a single smog season.

During the interval from May through October 1971, there were 13 days when peak oxidant concentrations exceeded 10 pphm on the same day at each of four South Bay BAAPCD stations: Redwood City, San Leandro, Fremont, and San Jose. Of these 13 days in 1971, 12 occurred in the months of September and October. In contrast, during September and October of 1972, oxidant values never exceeded 10 pphm at the four South Bay Stations during any one day.

The BAAPCD prepares monthly summaries of weather and pollution conditions within the district. Figure 1 shows the locations of BAAPCD stations around the South Bay Area where the houseboat experiments were conducted. The BAAPCD summaries document the highly unusual character of the weather and pollutant conditions prevailing during the fall season of 1972.<sup>5,6,7</sup>

A. September 1972

According to the BAAPCD:

Sunny but cool weather characterized September, with percentage of sunshine at San Francisco 10 percent above normal. Mean wind speeds were very close to monthly normals, and the ventilation index was slightly below. Mean maximum temperatures were almost 3°F below normal, and precipitation was above normal.

The State standards\* for carbon monoxide, sulfur dioxide, and nitrogen dioxide were not exceeded during the month. On the 21st, however, the highest hourly value of 0.23 ppm for nitrogen dioxide at San Jose did approach the standard.

The State 0.10 ppm hourly standard for oxidant was exceeded on 13 days, the lowest number for September in our 10 years of continuous record. Moreover, the greatest single high hourly value was 0.14 ppm at Vallejo on the 21st.

In the southern part of the Bay, where the experiments were conducted, Fremont and San Leandro showed the highest oxidant concentration (0.13 ppm) for the month. Fremont also had the highest number of days with oxidant levels equal to, or greater than, 0.10 ppm. Although

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\* The California State standards are: Oxidants - 0.1 ppm for 1 hour; carbon monoxide 40 ppm for 1 hour or 10 ppm for 12 hours; nitrogen dioxide - 0.25 ppm for 1 hour; sulfur dioxide - 0.5 ppm for 1 hour or 0.04 ppm for 24 hours; suspended particulate - 100  $\mu\text{gm m}^{-3}$  annual geometric mean.

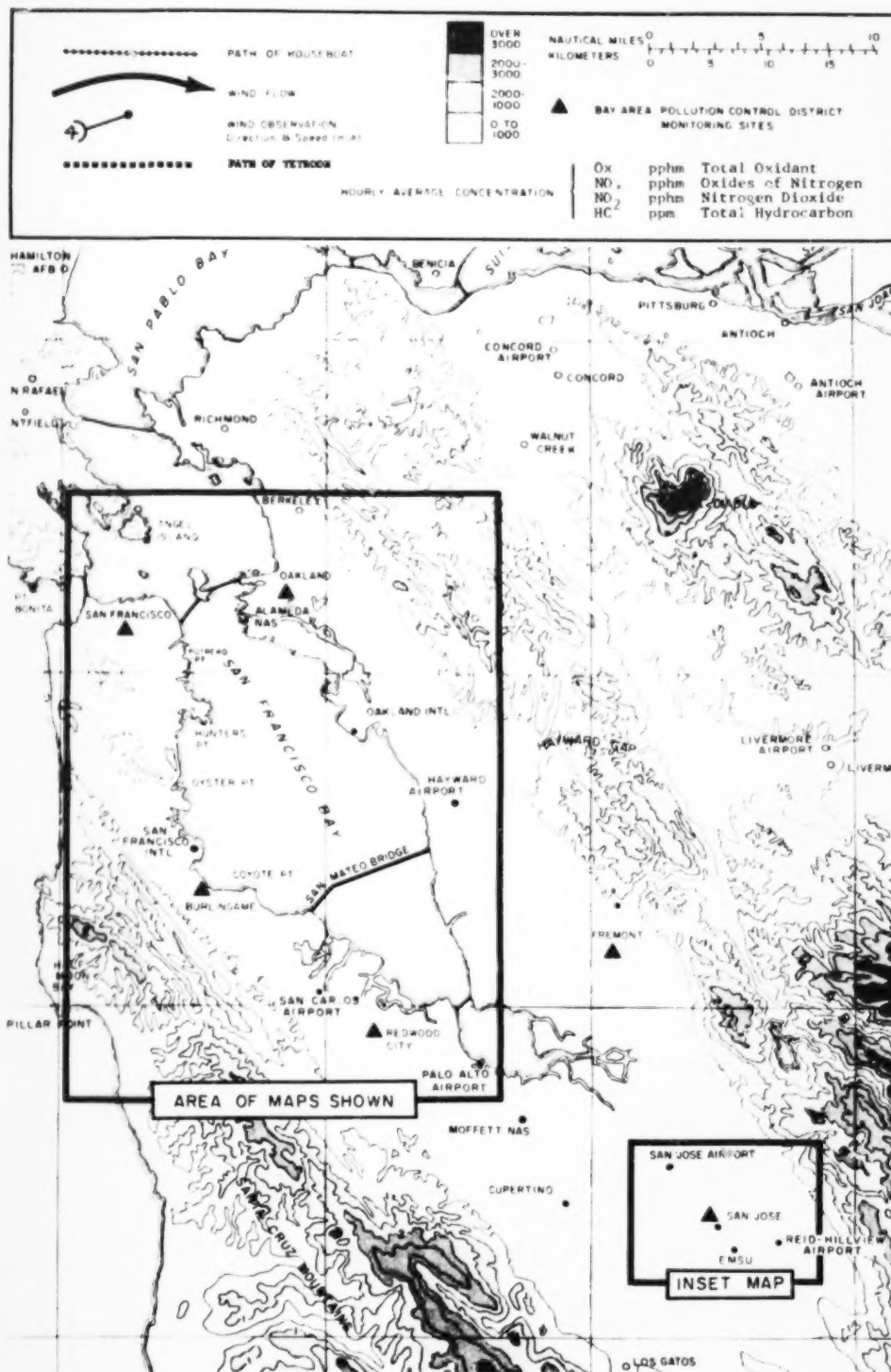


FIGURE 1 OVERALL AREA OF SAN FRANCISCO BAY WITH SAMPLING AREA INSET

there were 13 days in September when one or more stations of the total complement of BAAPCD stations recorded oxidant levels at or above 0.10 ppm, there were only seven days when one or more of the eight stations surrounding the southern part of the Bay had such concentrations. On September 12, Fremont and Redwood City each had high hourly readings of 0.10 ppm. On September 20 and 21, San Leandro reached 0.10 ppm on both days and Fremont reached 0.13 and 0.12 for those two days, respectively. On September 29, Fremont reached 0.11 ppm, San Leandro 0.13, and Oakland 0.12. No other days during the month had more than one station reach the 0.1-ppm oxidant level.

B. October 1972

The BAAPCD<sup>6</sup> describes the month of October as follows:

October of 1972 was the third wettest since the start of record at San Francisco in 1849, with precipitation more than 400 percent above normal. All-time October records were set for maximum hourly rainfall and for consecutive rainy days. Hours of sunshine were 20 percent below normal and mean maximum temperatures almost 3° F below normal. Wind speeds and ventilation were somewhat above their means. The stagnation periods which climatologically characterize October did not occur this year.

As a consequence of the protracted rains and good ventilation, this was the cleanest October since the start of continuous monitoring. State standards for carbon monoxide, sulfur dioxide, and nitrogen dioxide were not exceeded during the month.

There were only four days over the State 0.10 ppm oxidant standard this October compared with 23 in 1964, the worst season. Moreover, there were no days over the 0.15 ppm eye irritation level, and there were no 0.10 ppm days at 13 of our 20 oxidant monitoring stations. Most of the excesses occurred on October 5th, 6th, and 7th. With southerly airflow in this period the highest values were in the North District. Maximum high hour values were 0.13 at Napa on the 6th, and 0.12 at Santa Rosa on the 5th.

Around the southern part of the Bay, the 0.1-ppm oxidant standard was reached on only three days and at only three stations: San Leandro, Fremont, and Redwood City. These three stations reached 0.11 ppm on October 5, and the latter two reached 0.1 ppm on October 7. Fremont had a high reading of 0.1 on October 23.

C. November 1972

The last day of field observations was November 17. The last week of the month was relatively clear and sunny. However, according to the BAAPCD<sup>7</sup>, the month as a whole was characterized by:

...cold, wet, cloudy, windy conditions...The 6.40 inches of rainfall at San Francisco established the second highest monthly value in over a century of record, and the all-time 24-hour rainfall record was set on November 13-14. The average maximum temperature, almost 4° F below normal, was the all-time lowest November value of record. However, the final week of the month did bring a period of sunshine and high stability. The continuing rains and good ventilation resulted in generally clean air during the month.

No station in the district exceeded the oxidant standard in November before the end of the experimental period. Among the South Bay stations, the highest value reached was 0.07 ppm at Fremont on November 2.

D. Effects of Unusual Conditions

Appendix A describes the climatology of the San Francisco Bay Area and the expected weather conditions. The above summaries of 1972 autumn weather and pollutant conditions refer frequently to unusual occurrences. The emphasis in the preceding discussion was on pollutant concentrations and meteorological conditions conducive to high values of these concentrations, because high pollutant concentrations were one of the two major conditions deemed desirable for the planned experiments.

The other condition desired was the frequent occurrence of air trajectories passing over San Francisco, followed by long fetches over the open waters of the Bay. With the highly unusual atmospheric conditions discussed above, it is not surprising that the second type of hoped-for conditions also failed to materialize very often. Large-scale air motions from the northwest are typical of the San Francisco Bay Area in the autumn; these produce the desired trajectories. Such winds occurred infrequently in 1972. During the autumn of 1972, breezes often blew outward from the Bay all around its perimeter. During these intervals of onshore winds, the Bay appeared to be in an area of clear air relative to the surrounding landmass. Measurements on the houseboat indicated pollutant concentration levels similar to background levels in clean atmospheres.

East or west winds were also more commonly encountered than winds from the northwest. The northwest wind direction permits longer tracking of tetroons during sampling runs because the axis of the Bay lies northwest to southeast. Other wind directions, similar to those common during the 1972 smog season, severely restrict the tracking time or preclude the use of San Francisco as an emission source.

#### IV MEASUREMENT TECHNIQUES

##### A. General Operational Techniques

San Francisco Bay was selected as an area to study and define active photochemical processes because of the unique topography and consistent wind flow patterns that are typically present during meteorological conditions conducive to smog formation. The typical prevalent wind flow pattern that occurred during a four-year period was reported by Smalley<sup>6</sup> and a more recent wind study was reported by Meteorology Research Inc.<sup>7</sup> During the autumn, the prevalent wind flow pattern is one where marine air passes over San Francisco and then divides with a flow to the northeast and one to the southwest down the axis of the Bay. The prevalent wind flow pattern as reported by Smalley for the month of October is shown in Figure 2.<sup>8</sup> The clean marine air accumulates a burden of pollutants typical of a large urban source during passage over San Francisco and then flows down the axis of the Bay. There are no additional significant pollutant sources where fresh reactants are added to the atmospheric burden for distances of approximately 32 kilometers or more. Thus, under meteorological conditions conducive to smog formation, San Francisco Bay provides a location to study photochemical smog processes where addition of fresh reactants does not complicate data interpretation. Since the measurements are made in the real atmosphere rather than in laboratory test chambers, this type of study provides a link or a bridge between laboratory measurements and conventional aerometric surveys. The San Francisco Bay, under appropriate meteorological conditions, provides essentially a wall-less smog chamber in which transformation processes of smog constituents can be studied and

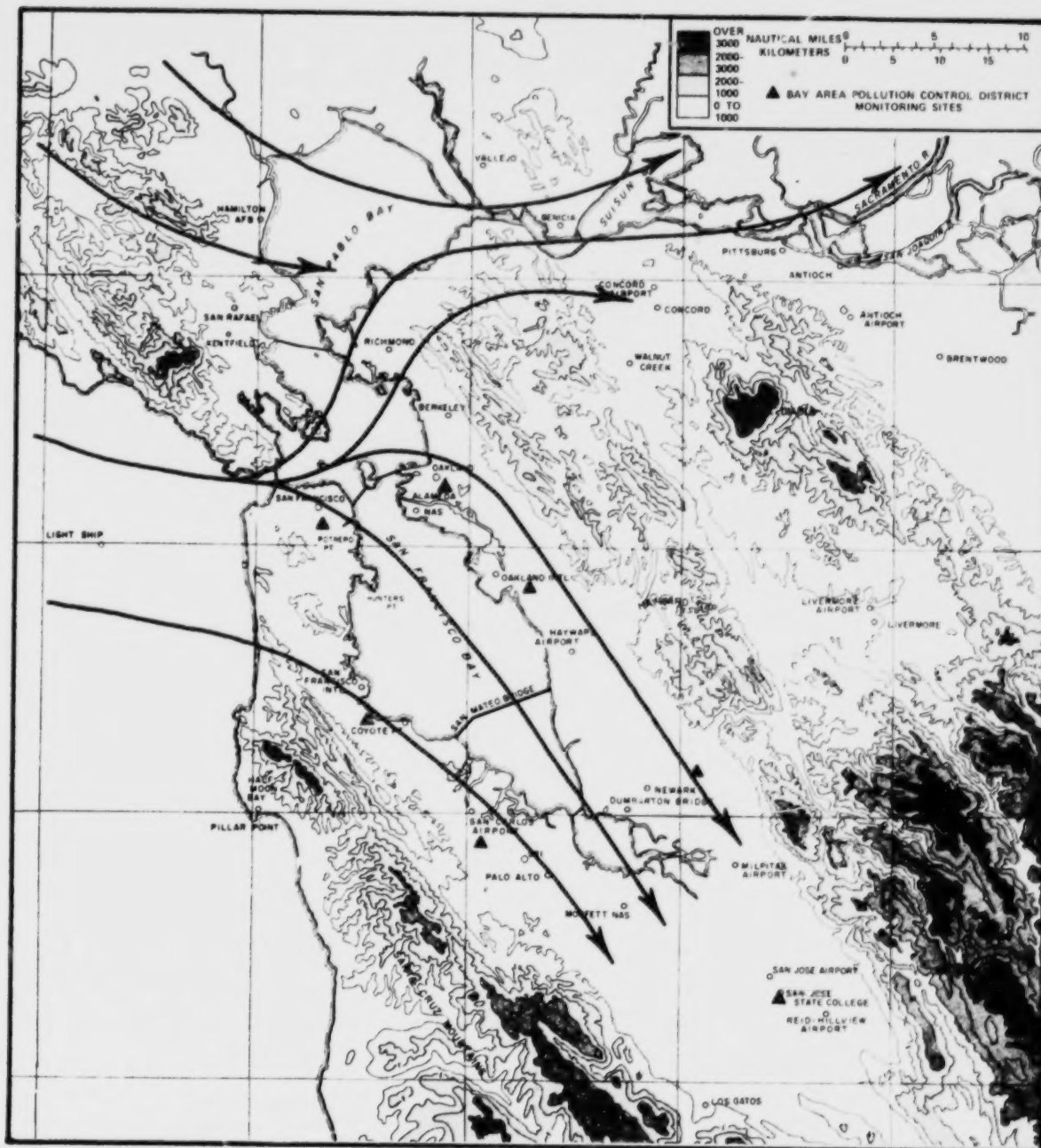


FIGURE 2 PREVALENT SURFACE WIND FLOW PATTERN FOR OCTOBER (Mean wind speed at San Francisco - 9 mph; Oakland - 6 mph)<sup>8</sup>

defined with less ambiguity than with either test chamber studies or previous aerometric studies.

This research project studied smog constituents using a Lagrangian approach where the changes of smog constituents due to aging and atmospheric influences were measured within a moving air parcel. A tetroon, a constant level balloon, was launched to mark a single parcel of air. The houseboat, was maintained in a position directly beneath the tetroon during its free flight over San Francisco Bay. Measurements were made of composition and concentration of atmospheric pollutants within the air parcel during movement down the Bay. In addition to the houseboat laboratory, an instrumented helicopter was used to obtain pollutant concentration gradients both vertically and horizontally with respect to the marked air parcel. Sampling runs where tetroons were followed were begun immediately downwind of a significant pollutant source. Background measurements of pollutant concentration and composition immediately downwind of the source were made prior to launch of the tetroon.

#### B. Mobile Laboratory - Houseboat

The houseboat used in this study was rented on a monthly basis and outfitted as a mobile laboratory. The boat was 12.5 meters in length with a 3.7 meter beam and a planing hull. The size and hull design provided a stable platform for the instrumentation. The craft was powered by twin 225-horsepower Chrysler inboard-outboard marine engines. The maximum cruising speed of the fully instrumented houseboat was about 24 km/hr. With the outdrives in normal position, the draft was 90 centimeters. The shallow draft permitted operation of the houseboat in shallow areas of the Bay. The boat was equipped with duplicate controls in the forward cabin and on the flying bridge. A VHF marine radio provided ship-to-ship-to-shore communication. A portable VHF transceiver operating on the aircraft intercom frequency (124.95 MHz)

was used for communication between the houseboat and the helicopter. The mobile laboratory was also equipped with a depth finder and inflatable life raft to ensure safety during operation.

It was vital to this research program to locate the position of the houseboat on the Bay at frequent intervals. Azimuthal sightings, made with a hand-held bearing compass, were used to obtain a position fix of the houseboat relative to known landmarks. By trial and error, a location was found forward of the flying bridge at which minimal deviation errors were introduced into azimuthal measurements taken by the hand-held bearing compass. This location was marked and used as a sighting location for all navigational fixes. However, even at this deck position, the steel hull and engines introduced a significant deviation to azimuthal readings made approximately 60 degrees to either side of the center line of the stern of the houseboat. To overcome this problem, at the beginning or end of each sampling run, the boat could be maneuvered so that fixes of any appropriate landmark could be made over the forward end. Even with these precautions, deviations introduced by the mass of the craft were larger than the errors associated with reading azimuthal angle on the hand-held bearing compass. Finally, a navigation compass was installed on the flying bridge, which compensated for the deviations introduced by the steel hull. A chart table complete with drafting machine was installed in the forward cabin of the houseboat so that the craft's position could be plotted on a chart during each sampling run.

During trial runs on the Bay, 24 landmarks located on and around the perimeter of the Bay were selected to serve as reference points for navigational fixes. These landmarks were coded as a three-digit alphanumeric designation so that navigational fixes could be entered onto the onboard data tape.

## 1. Air Quality Instrumentation

The air quality instrumentation installed aboard the houseboat, including instrumentation for aerosol measurements funded by the California Air Resources Board (ARB), is listed in Table 1. Appendix B gives details of the air quality instrumentation, calibration procedures, and analysis techniques. In addition to the air quality instruments, up to 10 compressed gas cylinders were mounted within or below the main cabin of the houseboat. An extremely stable source of 115 V, 60 Hz was required to power the data tape recorder and the computer. The 6-kVA motor generator aboard the houseboat did not provide adequate voltage of frequency stability for this application. Therefore, deep-cycle, lead-acid storage batteries in conjunction with an inverter were installed to power the tape recorder and computer. The batteries provided power for a period in excess of 8 hours and were recharged overnight by a battery charger.

The location of instrumentation and associated equipment in the interior of the houseboat was governed by two primary factors: (1) the houseboat could not be permanently modified, and (2) a reasonable distribution of weight had to be maintained so as not to jeopardize performance or safety.

Before fabrication of the sample inlet system, it was necessary to ensure that the location and height planned for the system would provide samples not contaminated with engine exhaust. A test run was therefore made in the houseboat using a hand-operated condensation nuclei (CN) counter while following a tethered balloon to establish an exhaust-free location and height. The sampling inlet to the CN counter was a length of 0.25-inch Teflon tubing supported on a telescoping pole that could be extended to 9 meters above the

Table 1

## PROJECT INSTRUMENTATION

| <u>Measurement</u>                                  | <u>Measurement Principle</u> | <u>Supplier and Model</u>             |
|-----------------------------------------------------|------------------------------|---------------------------------------|
| <u>Funded by Coordinating Research Council</u>      |                              |                                       |
| Ozone                                               | Chemiluminescent             | Bendix Model 8002                     |
| NO and NO <sub>x</sub>                              | Chemiluminescent             | Bendix Model 8101 B                   |
| Total hydrocarbon                                   | Flame ionization detector    | Beckman Model 400 A                   |
| Carbon monoxide                                     | Mercury displacement         | Bacharach Model US400L                |
| Carbon monoxide                                     | Nondispersive infrared       | Beckman Model 315AL                   |
| Turbidity                                           | Integrating nephelometer     | Meteorological Research<br>Model 1550 |
| Temperature                                         | Thermistor (dry)             |                                       |
| Relative humidity                                   | Thermistor (wet)             |                                       |
| Solar intensity                                     | Thermopile                   | Honeywell                             |
| Hydrocarbon distribution                            | Gas chromatography           | Hewlett Packard<br>Model 5750*        |
| <u>Funded by the California Air Resources Board</u> |                              |                                       |
| Total sulfur                                        | Flame photometric            | Meloy Model SA120                     |
| Condensation nuclei                                 | Continuous reading           | Environment/One,<br>Model Rich-100    |
| Particle size<br>distribution                       | 90° Light scattering         | SRI                                   |
| Total particulate                                   | Hi-vol filter                |                                       |
| Particulate distribution                            | Lundgren impactor            | Environmental Research                |

\*Two columns: C<sub>1</sub> to C<sub>3</sub> on 1/8 in. × 3 meters packed column on phenyl-isocyanate on Porasil C; C<sub>3</sub> to C<sub>10</sub> on 0.02 in. × 300 ft capillary column coated with squalane. Grab samples were collected cryogenically.

upper deck. It was found that the proposed sampling point 4 meters above the deck of the flying bridge next to the wheel was acceptable. Separate sample inlet lines were used for gaseous and particulate pollutants. All gas samples were collected through 0.25-inch diameter FEP Teflon tubing. Teflon fittings were used up through the O<sub>3</sub> and NO<sub>x</sub> sample take-off points. Beyond these inlets, stainless steel fittings and Teflon tubing were used. The particulate sampling line was 6.5 cm polyvinyl chloride pipe. The details of these sampling lines may be found in Appendix B.

## 2. Data Acquisition System

The automated digital data recording system developed during CRC/EPA Contract CAPA 3-68(1-69) was installed on the mobile laboratory to facilitate collection and processing of data acquired on the Bay study. This system accepts analog voltage inputs, digitizes them, and records the data on magnetic tape. Data are acquired at three rates--every 15 seconds, 30 seconds, and 4.7 minutes--to accommodate the various data rates of the onboard instrumentation. Pollutant measurements of O<sub>3</sub>, total hydrocarbon (THC), atmospheric turbidity (integrating nephelometer), CO, total sulfur, and CN are acquired at a 15-second rate and are stored in computer memory. Pollutant measurements of NO, NO<sub>2</sub>, total nitrogen oxides (NO<sub>x</sub>), dry and wet bulb temperatures, and solar intensity are acquired at a 30-second rate and stored in computer memory. The aerosol particle counter is interrogated every 4.7 minutes. At 5-minute intervals, the collected raw data stored in computer memory are recorded on magnetic tape. The computer, in addition, converts the raw data to engineering units, computes 5-minute averages, and prints a summary of the measurements by means of an onboard teletype. The computer's internal clock provides the time sequence required to

operate the program.

Computer software was developed to permit the time of each navigational fix, plus up to five observed azimuths of known landmarks, to be entered by teletype into the onboard computer. Thus, the navigational information could be recorded on magnetic tape concurrently with the air quality data. The computer will accept 24 landmarks coded as a three-digit alphanumeric designation. Inappropriately encoded entries and azimuths greater than 360 degrees are rejected by the computer.

### 3. Tetroons

The tetroons, purchased from Raven Industries, Sioux Falls, South Dakota, had a volume of 240 liters and were fabricated of 2-mil-thick orange Mylar. The inflated tetroons were too bulky to pass through doors or windows of the houseboat cabin. Therefore, canvas cover was fabricated to encircle the roof overhang forward of the main deck pilot house to provide a sheltered area for inflation and weigh-off of the tetroon. The houseboat was driven with the wind, at the speed of the wind, during weigh-off. This procedure provided the least turbulence within the tetroon shelter for weigh-off. The tetroons were overpressurized to ensure that the volume of the tetroon would not increase at operating altitude. A payload of aluminum pellets and steel BB shot was added until zero buoyancy was achieved. The free lift required to achieve flight at a particular altitude is given by:  $\ell = V(\rho_o - \rho_a)$ , where

$V$  - volume in  $\text{cm}^3$

$\rho_o$  = sea level air density in  $\text{g/cm}^3$

$\rho_a$  = air density at the selected altitude in  $\text{g/cm}^3$

$\ell$  = free lift in g.

The tetroon payload was then adjusted to allow the tetroon to float at an altitude of 60 to 120 meters.

The tetrooms were difficult to weigh to a reproducible positive buoyancy under field conditions. Although the operational technique described previously provided the least turbulence within the tetroom shelter, much more reproducible tetroom flight altitudes could have been attained through the use of a turbulence-free shelter. However, permanent modifications to the houseboat would have been required to significantly improve the facility for tetroom flight preparation.

#### C. Airborne Laboratory--Helicopter

The helicopter instrument package (Table 2) was designed initially for installation and operation in a Bell 47J-2A helicopter. Although total assembly, including operator, was within the rated load capacity of the 47J-2A, the performance of the aircraft was inadequate to ensure safe operation.

Table 2

#### HELICOPTER INSTRUMENTATION

| <u>Measurement</u>   | <u>Measurement Principle</u> | <u>Supplier and Model</u> |
|----------------------|------------------------------|---------------------------|
| Total oxidant        | Electrochemical              | MAST 724A                 |
| NO - NO <sub>x</sub> | Chemiluminescent             | Bendix Model 8101B        |
| Carbon monoxide      | Mercury displacement         | Bacharach US400L          |
| Temperature          | Thermistor                   | SRI                       |

Therefore, the instrument package was redesigned and assembled for use in the higher performance Bell Jet Ranger. The package was inspected and certified by the Federal Aviation Administration. The Bell Jet Ranger and the 47J-2A were available for use on short notice. The performance of the Jet Ranger was adequate in all aspects of the flight requirements. However, the cost per flying hour of the Jet

Ranger was \$240 per hour as opposed to \$145 per hour for the Bell 47J-A2.

The sampling inlet system of the airborne laboratory utilized 0.25-inch Teflon tubing and fittings. The inlet was attached to the outside of the helicopter cabin, passed through the window, and was connected to a glass and Teflon manifold. The manifold was vented to the cabin to relieve the ram pressure built up in the system by the forward velocity of the helicopter.

The Jet Ranger had 100 A at 24 V from the alternator, of which 80 percent was available to power sampling instruments (the 47J-2A had only 50 A total power). A 1-kW Topaz inverter provided 110-V power at 60 Hz for the sampling instruments. The airborne measurement data were recorded with a four-channel inkless strip chart recorder.

#### D. Operation of the Mobile Laboratories

The operating crew of the houseboat consisted of four people on sampling days without helicopter airborne measurements. The crew functions for the houseboat were as follows:

- Guidance of the houseboat and direction of experiments
- Instrumentation monitoring and operation of data acquisition system
- Operation of onboard gas chromatograph
- Navigation.

When the helicopter was operating, one additional houseboat crew member was required in addition to the operator aboard the helicopter. This additional observer recorded the location of the helicopter with respect to time and the houseboat.

The operating personnel of the houseboat and helicopter were continuously on standby during the smog season and available to

operate the mobile laboratory on short notice. The manning and operation of the houseboat had priority over all normal assignments and commitments of the project team members. Although backup team members were designated, they were seldom required to substitute for the operating boat crew.

The houseboat was berthed at the Port of Redwood City during outfitting of the craft as a mobile laboratory. This location, about 13 kilometers from SRI, provided convenient access for SRI personnel and equipment during the installation phase. During the operational phase of the research project, the houseboat was berthed at Oyster Point Marina, South San Francisco. The selection of Oyster Point Marina for a permanent berth during the operational phase was based on several criteria. First, the over-water travel time was 45 minutes or less to either San Francisco or the East Bay. Second, the facilities at Oyster Point were well suited for operating a research craft. There was ease of access to the houseboat for heavy equipment, ample parking, and water and power to each berth. Third, the vehicle travel time from SRI was 45 minutes or less.

The helicopter used for this research program was based at Oakland International Airport. The instrument package was installed and removed after each flight.

The BAAPCD routinely forecasts smog potential on a short-term basis; however, these forecasts are developed to predict the occurrence of moderate to heavy pollution. During a smog season like 1972, with atypical meteorological patterns, the basis for developing accurate forecasts was inadequate. Therefore, accurate forecasts could not be developed by either the BAAPCD or SRI.

The BAAPCD was contacted on a daily basis to ascertain the peak concentrations of total oxidant, NO<sub>2</sub>, and CO recorded at monitoring

stations in Redwood City and San Jose. This daily contact was initiated on 21 August 1972, and a log was maintained throughout the smog season. The pollutant concentrations and the hour when peak concentrations occurred were obtained by 1630 on the same day the measurements were made. This information permitted evaluation of the trends of photochemical activity in sufficient time to plan operation of the mobile houseboat laboratory for the following day. In addition, both long-and short-term weather forecasts were obtained from the U.S. Weather Bureau on a frequent basis. On days when the meteorological conditions were predicted to be appropriate for photochemical smog formation, Mr. Sandberg of the BAAPCD was consulted to obtain a supplementary forecast evaluation for smog potential.

The temperatures and wind direction at various altitudes were obtained from the Upper Air Group at the Oakland Airport. The Oakland Airport meteorological soundings provided information about the depth of the mixing layer, upper air wind directions and speeds, and stability of the inversion when it was present.

To conserve resources, the houseboat was frequently activated without simultaneous activation of the helicopter. Several factors influenced this operational approach. First, the helicopter was expensive to operate(\$240 per hour plus the expense of the instrumentation operator). Second, the lead time to activate the helicopter was longer than that required to activate the houseboat. Third, on some occasions the helicopter was not available for operation on a specific day because of maintenance requirements or because a pilot was not available at the time. During the latter portion of the smog season, visual observations of the Bay area were made at sunrise (from the home of one of the crew members) to supplement the smog potential forecasts. On the basis of these visual observations, the houseboat crew was frequently contacted by telephone, and the houseboat was activated.

It would be underway and operational within 2 hours after the decision to activate.

When the houseboat reached a position beyond the entrance to Oyster Point Harbor, it was stopped, and a small weighted, helium-filled balloon was released to determine wind direction and speed. On the basis of the observed wind direction and predicted meteorological conditions, a tentative tetroom launching site was selected. During transit to the selected tetroom launching site, marker balloons were released periodically. Although precautions were taken to maintain a heading into the wind while releasing these marker balloons, there was a possibility of inadvertent exhaust contamination during the short interval when the houseboat was nearly motionless.

Once the final location for launching the tetroom had been selected, the tetroom was weighed off using the procedures described in Section B.1.C. Exhaust gas contamination resulted prior to each tetroom run during this interval. Therefore, the pumps for the particulate filter samples were shut off so that the integrity of these collections would not be compromised. The remainder of the air quality instruments were left in an operating mode because the sample line residence time was short. The houseboat was maneuvered into the wind to provide a contamination-free atmospheric sample for both the gaseous and particulate samplers prior to tetroom launch. The houseboat was steered at a course 60 degrees to 90 degrees away from the direction that the tetroom would travel at the moment of launch to obviate exhaust gas contamination. Then the houseboat was maneuvered in a circular path back to the trajectory of the tetroom at a speed greater than the wind until a position was reached directly beneath the tetroom. The houseboat was then slowed to reduce the surface speed to equal the flight speed of the tetroom.

While the houseboat maintained a speed equal to that of the tetroon, staying beneath the tetroon, the wind speed was measured by an anemometer at the bow end of the flying bridge. The measured forward wind speed was about 1 m/sec during tracking. Thus, the wind shear was about  $-0.01$  m/sec/m. The surface to tetroon wind speed differential seemed to be reasonably consistent, providing the tetroon speed exceeded about 2 m/sec. Due to this surface boundary layer wind shear, the houseboat continuously moved faster than the air at the surface and encountered both air mixing down from above and new air at the surface, when moving directly under a tetroon-marked air parcel.

At the times when obvious exhaust gas contamination occurred, simultaneous increases were observed in the concentration of NO, CO, and CN. Frequently during intervals when tetroons were tracked by the houseboat, marked changes occurred in NO concentrations within short intervals of time. No corresponding increase in CN or CO occurred to suggest exhaust contamination. In other instances, changes occurred in CN without corresponding changes in CO and NO concentration. Similar observations were made during traverses of the Bay at high speeds where exhaust contamination from the houseboat could not contribute. Underwater exhaust gas exit ports, as used on the houseboat, are not likely to provide any scrubbing mechanism that would preferentially remove CN or CO without significantly reducing NO concentrations. These observed changes in NO concentrations and CN are thus probably real and indicate the inhomogeneity of pollutant distribution over the Bay.

Although the approach to tracking tetroons under a variety of wind speeds had been planned in advance, much innovation was required in the field to select the most satisfactory approach for a particular tetroon release. Several tetroon runs were made during intervals when the wind patterns offshore had not stabilized. During these sample

runs, the course of the tetroom varied greatly in direction and speed during the flight interval. If the speed of the tetroom did not exceed about 2 m/sec, one of the engines of the houseboat would be turned off during the run to minimize the volume of exhaust gases emitted. At very slow tetroom speeds, contamination by exhaust gases could not be eliminated without incorporating additional precautions in the tracking procedure. During these intervals of very slow speed tracking, a helium-filled balloon was tethered to the flying bridge of the houseboat to float a few feet above the sample intake. The tethered balloon was used as an indicator to ensure that the houseboat always maintained a forward speed relative to the wind. The tetroom was tracked by maneuvering a series of figure-eight patterns perpendicular to the path of the tetroom with the cross-over point of the figure eight below, but slightly behind the floating tetroom. The turns at the ends of the figure eights were made by turning upwind in each instance. The figure-eight pattern extended some 100 to 150 meters to each side of the tetroom flight path.

The decision to activate the helicopter mobile laboratory was made on the basis of either predicted meteorological conditions or the pollutant measurements observed in the morning from the houseboat. The helicopter instrument package was located at Butler Aviation Company at San Francisco Airport, who also provided access to line power for instrument warm-up. The airborne instruments were turned on to warm up for 1 to 2 hours prior to installation in the helicopter. The airborne instruments were usually activated by a member of the houseboat crew prior to activation of the houseboat mobile laboratory. The airborne instrument package was stored on a pallet jack along with two 12-volt batteries. After the helicopter had landed at Butler Aviation from its Oakland base, the airborne instruments were

disconnected from line power and transferred to battery power. The instrument package was then moved manually to the helicopter. The instrument package was elevated to the floor of the helicopter, moved into place, and secured. The instrument package was then transferred from the batteries to the helicopter power supply. At the conclusion of each flight the operation was reversed, with the instrument package stored unpowered until the next flight.

The helicopter mobile laboratory provided three types of pollutant concentration and temperature gradient measurements to supplement those measurements made by the houseboat laboratory:

- Vertical Profiles--The measurement of the vertical gradients of pollutant concentrations and temperature gradients was accomplished by performing a slow, vertical ascent spiral over or near a known landmark. The vertical profiles began near the surface (30 meters altitude or less) with an ascent rate of about 30 meters per minute to an altitude of 150 meters. During the interval from 30 to 150 meters, the ascent was usually performed stepwise in 30 meter increments. Above 150 meters and below 300 meters, the helicopter ascended at the rate of about 60 meters per minute. Above 300 meters, the helicopter ascent rate was accelerated because only the temperature profiles are of major interest at altitudes in excess of 300 meters.
- Horizontal Traverses--The measurement of horizontal pollutant concentration gradients was accomplished by traverses upwind of the tetron launch site and parallel to the tetron flight path. Zigzag flight patterns were also made to obtain measurements of the spatial distribution of pollutants over the Bay. The flight paths of the helicopter during specific sampling days are shown in Appendix C.
- Airborne Tracking of the Tetron--Both horizontal and vertical pollutant concentration gradients were measured in the vicinity of the tetron during flight. The helicopter flew in a circular pattern around the tetron, maintaining the same altitude as the tetron, as it ascended to operating altitude. During each circle of the tetron, the instrument operator in the helicopter noted on the recorder chart the location where the helicopter compass indicated north. The

helicopter maintained a constant air speed of 30 or 40 mph. The helicopter observer of the houseboat crew noted in a log the exact time, synchronized with the houseboat computer clock, when the helicopter crossed the line of sight from the houseboat to a known landmark. The radius of the helicopter circles based on a constant speed and the time required for completion of a circle, varied from 200 meters to 500 meters with an average radius of 300 to 400 meters.

The usual operating procedure consisted of tracking the tetroon from launch to the estimated midpoint of the tetroon flight. Horizontal traverses were made during the midportion of the tetroon flight to determine pollutant concentration gradients. The helicopter returned to the tetroon for the remainder of the sampling run. Vertical profiles were usually undertaken prior to, or immediately following, a tetroon flight.

## V PRESENTATION AND INTERPRETATION OF THE DATA

### A. Overview of the Sampling Days

This section contains maps displaying streamlines, houseboat sample paths, tetron paths, pollutant concentrations reported by the BAAPCD, and pertinent wind speed and direction data of four selected sampling days. In Appendix C are maps of the remaining sample days that showed significant pollution. These maps graphically illustrate the hourly meteorological conditions encountered on sampling days during intervals preceding and succeeding tetron runs or other intervals of interest. Rawinsonde observations for the sample days are also included in this section and in Appendix C. The measurement data obtained by the houseboat mobile laboratory during all sampling days have been consolidated, edited, and recorded on a single reel of magnetic tape. This data tape is included as part of this final report. The contents of the data tape and the format are described in Appendix D.

Following is a brief summary of representative sample days, including tetron tracking intervals and the course of the houseboat. A capsule summary of all sampling days is given in Table 3.

- September 21<sup>\*</sup> --A tetron was released at 1030 on the north side of the Bay Bridge between San Francisco and Treasure Island. The tetron drifted slowly toward San Francisco, drifted south within 300 meters of the shore, and then drifted back over the Bay at 1056. The houseboat passed under the Bay Bridge at 1050. At 1100 the houseboat was again beneath the tetron and tracking resumed (1100 to

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<sup>\*</sup> All times are Pacific Standard Time (PST).

Table 3  
SUMMARY OF SAMPLING DAYS

| Date<br>(1972) | Time (hr:min) |      | Follow<br>Tetron | Heli-<br>copter | Houseboat Course                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
|----------------|---------------|------|------------------|-----------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                | Start         | Stop |                  |                 |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
| 9/21           | 0835          | 1030 | N                | N               | * OP to SF* to point just north of BB.<br>Tetron went over SF, then south over west side of Bay.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
|                | 1030          | 1235 | Y                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
| 9/30           | 0630          | 0850 | N                | N               | OP to SF. Drifted south of BB. Checked operation of instruments.<br>Returned to OP.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
|                | 0850          | 0930 | N                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
| 10/6           | 0620          | 0742 | N                | N               | * OP to HP, then to OA.<br>Tetron moved north along east side of Bay. Lost near Alameda.<br>Alameda to BB near SF.<br>Tetron moved south west side of Bay. Over land near HP.<br>Same path as 1208-1240.<br>Returned to OP, refueled, and headed for center of Bay.<br>Tetron headed south to SMB. Lost over shallow water.<br>Passed under SMB.* Tetron in sight but far away over shallow water.<br>OP to HP, then southeast to Alameda.<br>Tetron, moved north on east side of Bay. Lost over Alameda.<br>Headed for center of Bay. Helicopter instruments inoperative.<br>Tetron moved from center of Bay to OA.<br>OP slowly to SF near Ferry Building, just north of BB.<br>Returned to OP. Refueled. Summary from 0950 to 1056 not available.<br>Tetron moved from OP east northeast to OA.<br>Returned to OP.<br>OP to HP, then to middle of the Bay.<br>Tetron released but port engine clutch failed. Forced return to OP. |
|                | 0742          | 0835 | Y                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 0920          | 1056 | N                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 1056          | 1140 | Y                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 1230          | 1300 | Y                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 1300          | 1446 | N                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 1446          | 1526 | Y                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 1526          | 1545 | N                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 0615          | 0832 | N                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 0833          | 0905 | Y                | Y               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
| 10/7           | 0908          | 1035 | N                | Y               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 1035          | 1124 | Y                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 0622          | 0828 | N                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 0828          | 0930 | N                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
| 10/19          | 1041          | 1120 | Y                | Y               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 1120          | 1220 | N                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 0955          | 1152 | N                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|                | 1153          | 1216 | N                | N               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |

Table 3 (Continued)

| Date<br>(1972) | Time (hr:min) |      | Follow<br>Tetron | Heli-<br>copter | Houseboat Course                                                         |
|----------------|---------------|------|------------------|-----------------|--------------------------------------------------------------------------|
|                | Start         | Stop |                  |                 |                                                                          |
| 10/25          | 0545          | 0700 | N                | N               | OP to San Leandro.                                                       |
|                | 0700          | 0753 | N                | N               | Held position near San Leandro.                                          |
|                | 0754          | 0855 | Y                | Y               | Tetron moved east to OP.                                                 |
|                | 0855          | 1000 | N                | N               | Returned to San Leandro, refueled.                                       |
|                | 1045          | 1134 | N                | N               | San Leandro to 1 mi north of center of SMB.                              |
|                | 1135          | 1220 | Y                | Y               | Tetron moved west to Coyote Point. Helicopter followed for extra 0.5 hr. |
|                | 1221          | 1406 | N                | N               | Returned to OP.                                                          |
| 10/26          | 0600          | 0707 | N                | N               | OP slowly to north of BB near SF.                                        |
|                | 0708          | 0905 | N                | N               | Monitored pollutants in vicinity of SF.                                  |
|                | 0906          | 0948 | Y                | Y               | Tetron moved from SF to Berkeley.                                        |
|                | 0950          | 1140 | N                | Y               | Refueled at Berkeley. Wind off SF too strong. Returned to OP.            |
|                | 1040          | 1351 | N                | N               | OP to OA, then to HP.                                                    |
| 10/31          | 1352          | 1407 | Y                | Y               | Tetron moved from shore north of HP to Alameda.                          |
|                | 1408          | 1500 | N                | N               | Returned to HP. Wind strong. Returned to OP.                             |
|                | 0830          | 1120 | N                | N               | OP slowly to OA, then south to center of SMB, then north 1 mi.           |
|                | 1123          | 1317 | Y                | Y               | Tetron moved from center of Bay south over SMB center span.              |
|                | 1326          | 1400 | N                | Y               | Returned to OP to refuel.                                                |
| 11/2           | 1438          | 1633 | N                | N               | OP to HP to Alameda to SF. Engine ignition trouble repaired.             |
|                | 1635          | 1657 | Y                | N               | Tetron moved west from SF to Alameda.                                    |
|                | 1658          | 1738 | N                | N               | Alameda to HP. Wind strong, returned to OP.                              |
|                | 1038          | 1201 | N                | N               | From OP headed east, then southeast to 2 mi. north of SMB.               |
|                | 1218          | 1253 | Y                | Y               | Tetron headed south over SMB.                                            |
| 11/6           | 1254          | 1405 | N                | Y               | Returned to OP.                                                          |

Table 3 (Concluded)

| Date<br>(1972) | Time (hr:min) |      | Follow<br>Tetron | Heli-<br>copter | Houseboat Course                                   |
|----------------|---------------|------|------------------|-----------------|----------------------------------------------------|
|                | Start         | Stop |                  |                 |                                                    |
| 11/17          | 1030          | 1115 | N                | N               | OP to San Leandro Harbor for refueling.            |
|                | 1227          | 1308 | N                | N               | San Leandro to point midway between HP and OA.     |
|                | 1317          | 1347 | Y                | N               | Twin tetron release. Lost over OA. Returned to OP. |

Note: Incomplete data were also collected on 07, 11, and 13 September.

N = No.

Y = Yes.

n.a. = not available.

\*

OP = Oyster Point; SF = San Francisco; BB = Oakland-S.F. Bay Bridge; SMB = Hayward-San Mateo Bridge;  
HP = Hunter's Point; OA = Oakland Airport.

1235). The tetron was tracked during a flight trajectory down the middle of the Bay at an average speed of about 9.0 km/hr until the tetron descended to the houseboat at 1235. The meteorological conditions for 21 September closely approached the "ideal" conditions for marking and monitoring a single air parcel. The pollution levels on this day were the highest observed during the course of the project.

- October 6--A tetron was released near Oakland Airport and was tracked for 1 hour (0742 to 0835). The onshore breezes developed a northerly component after 1000. Two tetrons were released downwind of San Francisco (1056 to 1140, and 1230 to 1300). The northerly wind component did not become established and onshore breezes were reestablished. Another tetron released south of Hunters Point was tracked to shallow water off Coyote Point (1446 to 1526). Although the north wind appeared established at tetron launch, wind speed deteriorated to stagnation conditions, followed by onshore breezes. Low pollutant levels and variable winds characterized this sample day.
- October 7--Onshore breezes again dominated the early morning hours. A tetron was released with an anticipated fetch toward San Francisco (0833 to 0905), but the sample run terminated because of onshore breezes. A tetron released near the Bay center was tracked for about 45 minutes (1035 to 1124). A sudden front entered the area accompanied by high winds, which ended the sample day. October 7 was characterized by low pollutant levels and unusual meteorological conditions.
- October 19--Background measurements were made off San Francisco (0825 to 0843). A tetron released near Oyster Point was tracked to Oakland Airport (1041 to 1120). The helicopter was operational during the tetron run. The Bayshore Freeway and South San Francisco provided the upward pollution sources. This day was characterized by west winds and low pollution levels.
- October 24--A tetron run was attempted south of Treasure Island but failed due to the high wind velocity. The high chloride-to-sulfur ratio in the collected particulate is evidence that clean marine air was sampled in the absence of contributions to photochemical smog.

- October 25--The houseboat laboratory mapped pollutant concentrations from Oyster Point to Oakland Airport (0545 to 0627). A tetroon run was made from Oakland Airport to Oyster Point (0754 to 0855). The helicopter was operational during this run. The houseboat again mapped pollutant concentrations from Oyster Point to Oakland (0915 to 0957). The three traverses were over nearly identical paths. A tetroon was released north of the San Mateo Bridge (1135 to 1220). The helicopter was operational during this tetroon run. The houseboat then proceeded north to map pollutant concentrations (1215 to 1400). This day was characterized by an established east wind in the morning, deteriorating to onshore breezes in the afternoon. Pollution was light, but evidence of photochemistry was observed.
- October 26--Background pollutant concentration measurements were made immediately downwind of San Francisco (0716 to 0905). A tetroon was released and tracked from San Francisco to Berkeley (0906 to 0948). The helicopter was operational but little data are available due to instrument malfunction. This day was characterized by variable pollutant concentration but little evidence of photochemistry.
- October 31--A tetroon launched off Hunters Point was tracked to Alameda (1252 to 1407). The helicopter was operational during this tetroon run. This day was characterized by low pollution levels with relatively high wind speeds.
- November 2--The houseboat mapped pollutant concentrations during the morning, when the winds were variable, from Oyster Point to San Leandro Harbor (0830 to 0954). A tetroon was released and tracked from mid-Bay to south of San Mateo Bridge (1123 to 1317). The houseboat refueled and moved to Alameda (1438 to 1520). A tetroon released near San Francisco traveled to the Alameda Naval Air Station (1635 to 1657). Although the pollution levels were relatively high, the tetroon flight was of such limited duration that photochemistry was not observed. November 2 was characterized by light to moderate pollution with meteorological conditions approaching those suitable for measurement.

- November 6--The houseboat departed Oyster Point at 1025 with nearly calm winds. A tetron was released north of San Mateo Bridge (1218 to 1253). The helicopter was operational during this tetron flight and continued tracking the tetron after the houseboat terminated tracking. Pollutant concentrations were low with minimal photochemical activity on this day.
- November 17--The houseboat mapped pollutant concentration from Oyster Point to San Leandro Harbor (1030 to 1115). Two tetrons released simultaneously at mid-Bay between Hunters Point and Oakland Airport (1317 to 1347) floated at about the same altitude and within 60 meters of each other for the first 10 minutes. They were separated by 90 to 120 meters at the termination of the run at 1347. The wind speed during this run was about 2 m/sec. This day was characterized by variable winds and low pollution.

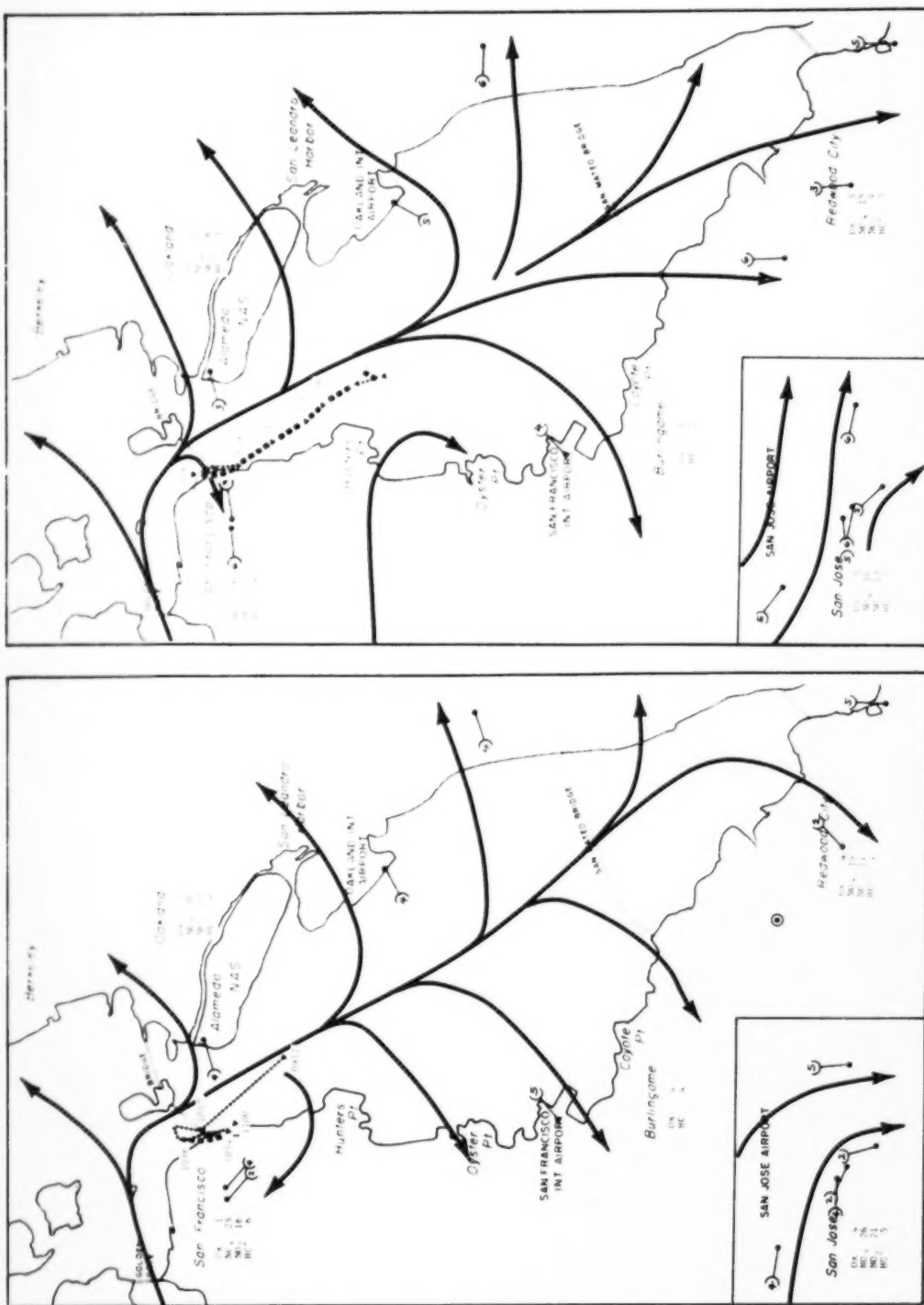
#### B. Selected Sampling Days

Four days were selected for detailed analysis. The following sections give a summary analysis for each day, including graphical presentations of meteorological conditions, houseboat and tetron paths, and pollutant concentrations. For convenience of the reader, only a summary is presented in the body of the report. Additional supporting information for users of these data will be found in Appendix E.

##### 1. 21 September 1972

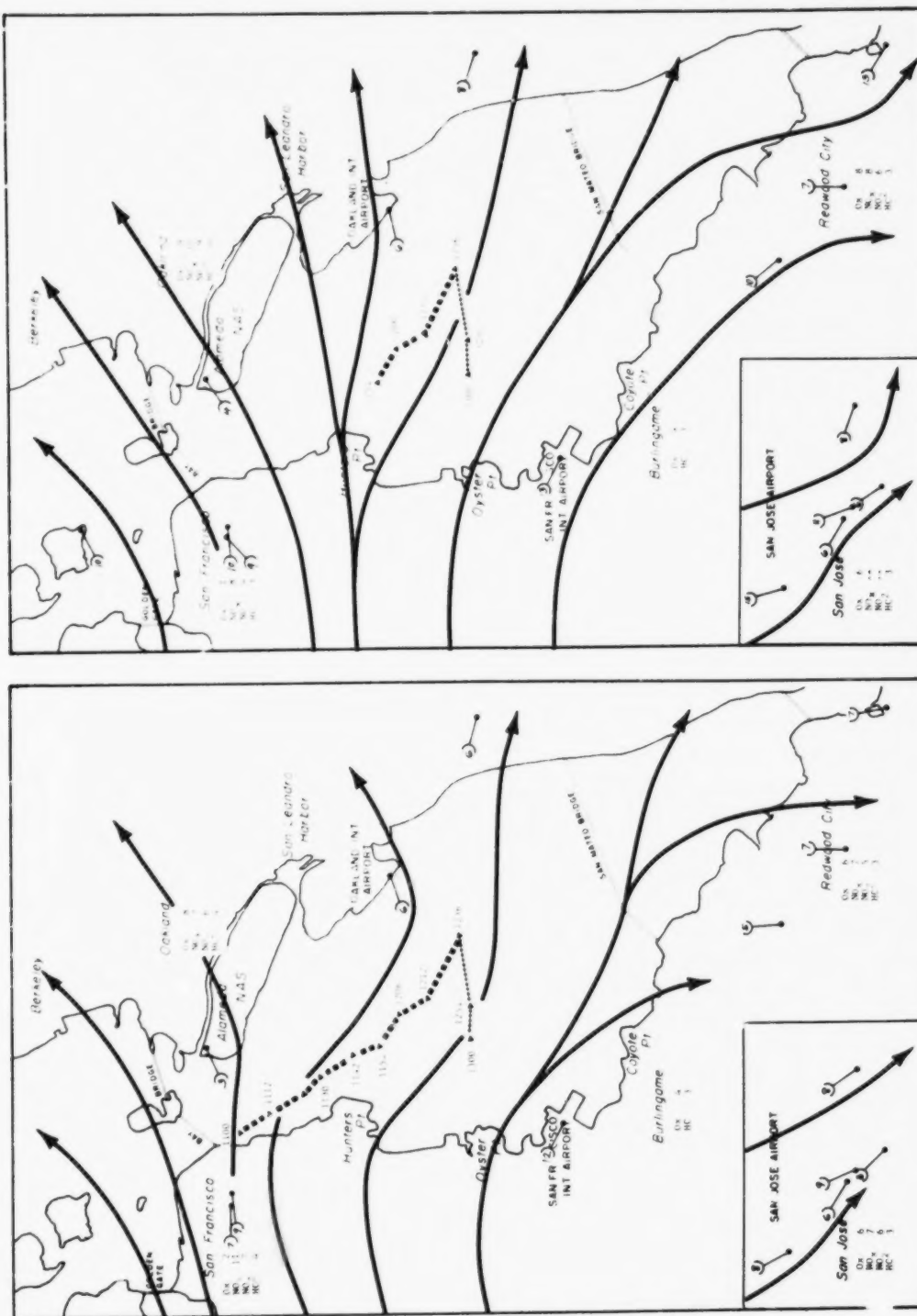
This day was selected because the tetron run occurred under almost ideal conditions. The tetron launched downwind of San Francisco was tracked for over 2 hours down the axis of the Bay. The pollution levels were the highest observed during the operational period of the mobile laboratories.

Figures 3 through 6 are maps illustrating wind flow patterns, houseboat sampling paths, tetron trajectories, rawinsonde observations,



(a) 1000 PST (b) 1100 PST

FIGURE 3 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 21 SEPTEMBER 1972



(c) 1200 PST

(d) 1300 PST

FIGURE 3 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 21 SEPTEMBER 1972 (Concluded)

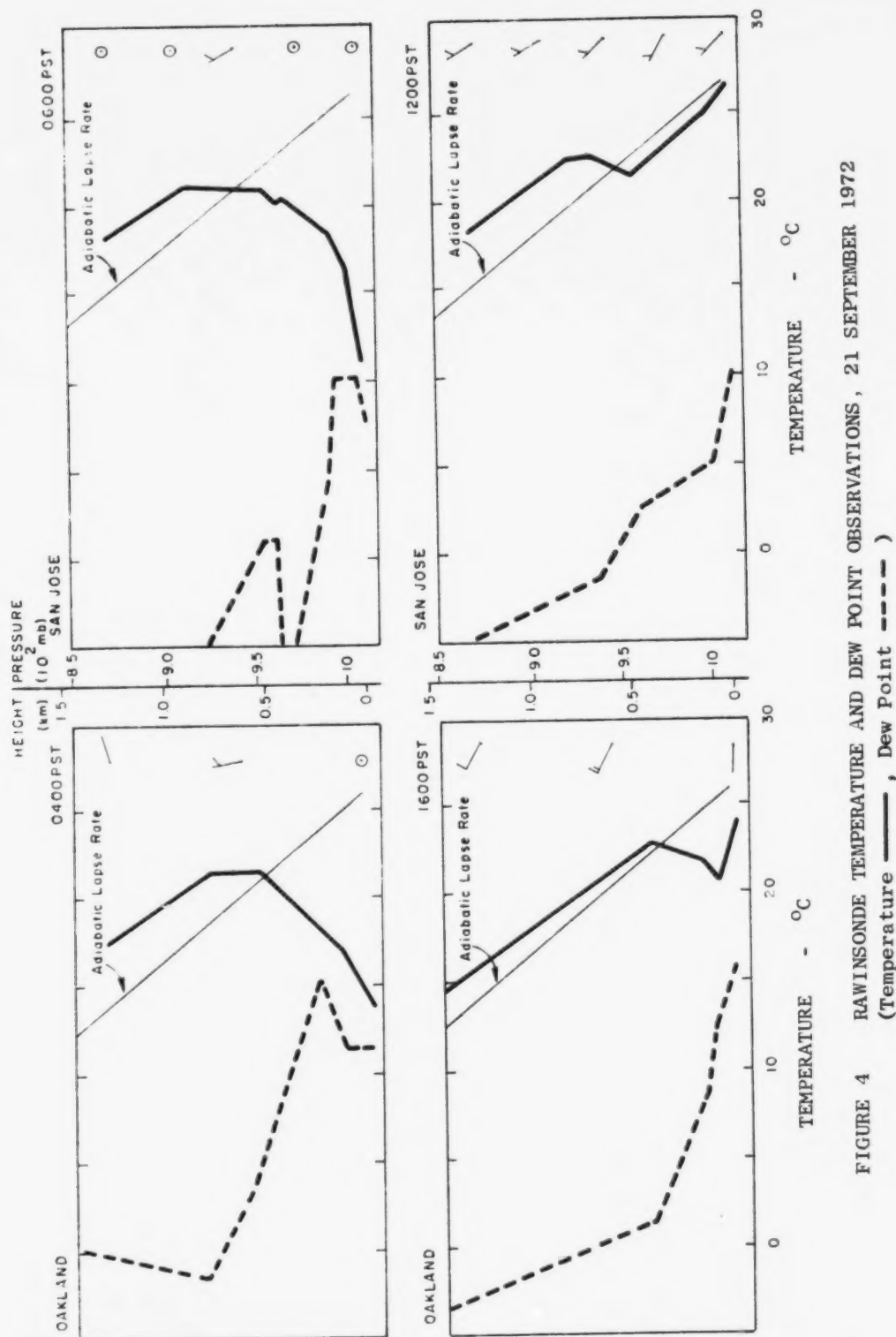


FIGURE 4 RAWINSONDE TEMPERATURE AND DEW POINT OBSERVATIONS, 21 SEPTEMBER 1972  
(Temperature —, Dew Point ----)

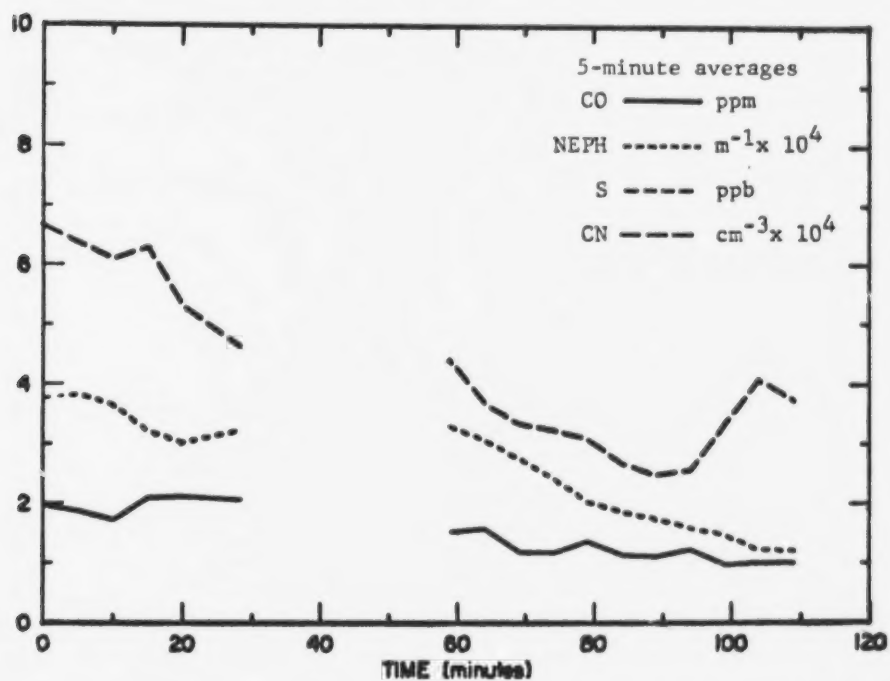
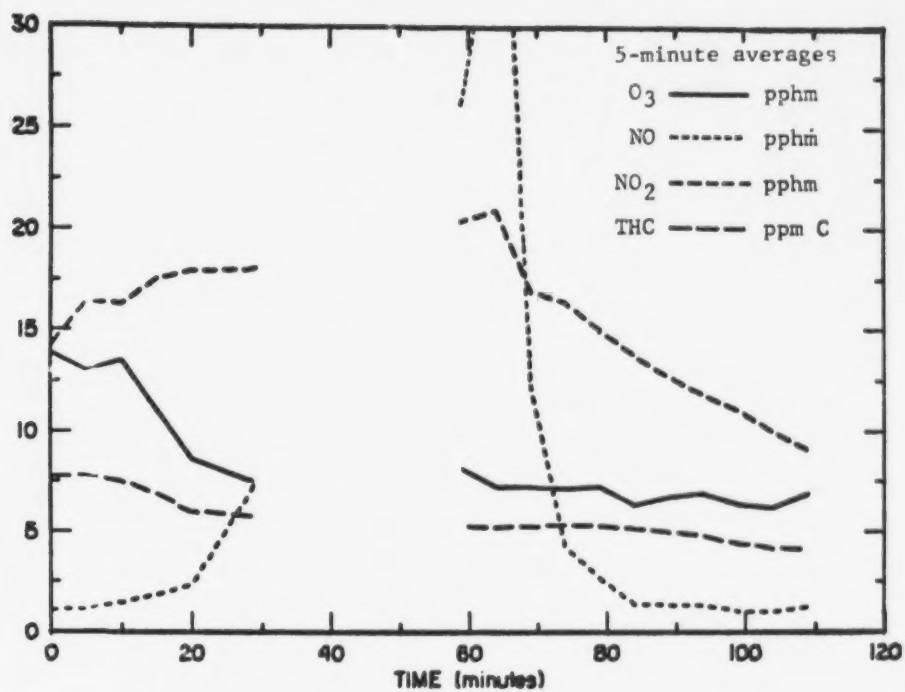


FIGURE 5 POLLUTANT CONCENTRATIONS OBSERVED DURING TETROON RUN, 21 SEPTEMBER 1972, 1037 to 1226 PST

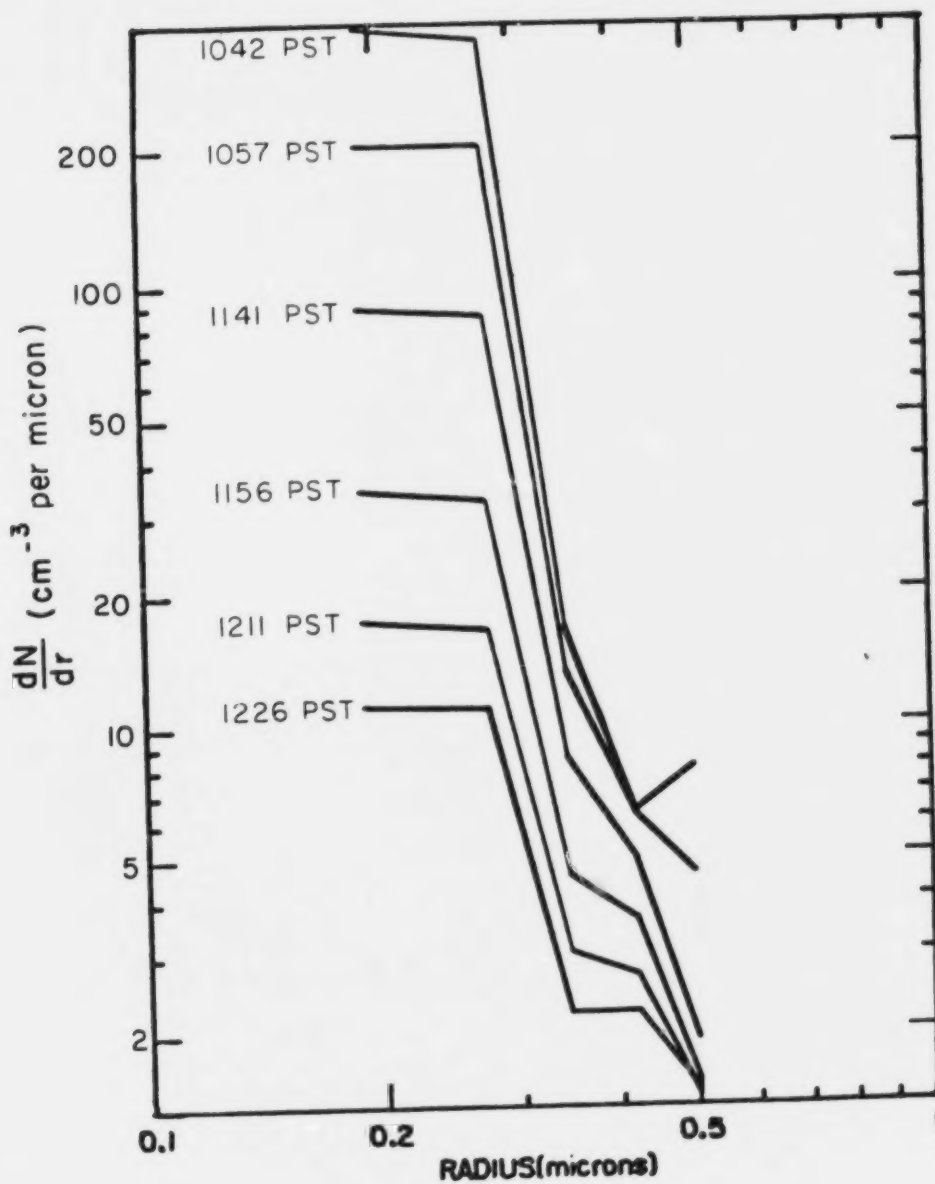


FIGURE 6 AEROSOL PARTICLE COUNTER DATA FOR VARIOUS AVERAGE TIMES, 21 SEPTEMBER 1972

pollutant concentrations, and aerosol particle data. The morning soundings for Oakland and San Jose showed a strong surface-based inversion extending to 0.5 kilometers thick isothermal layer causing very stable conditions. The noon San Jose soundings and the afternoon Oakland sounding showed that the inversion persisted throughout the day.

Meteorological observations showed calm or light winds around San Francisco during the early morning hours. From about 0900 to 1100, southeasterly air flow was observed in San Francisco; the winds in the South Bay were predominantly onshore so that wind direction was dependent on shoreline orientation. Between 1200 and 1300, a strong westerly sea breeze developed and rapidly blew the polluted air out of the Bay Area.

Samples collected near Hunter's Point from 0915 to 1000 indicated that the air mass was well aged and that substantial pollution levels were present ( $\text{NO} \sim 5$  pphm,  $\text{NO}_2 \sim 15$  pphm,  $\text{O}_3 \sim 4$  pphm). Therefore, the houseboat was moved to a location about 1 mile north of the Bay Bridge and 1 mile east of San Francisco and a tetroon was released (1030). The concentration of NO averaged 6 pphm,  $\text{NO}_2$  averaged 15 pphm, and  $\text{O}_3$  averaged 5 pphm. The ratio of NO to  $\text{NO}_2$  was low, a characteristic of well-aged smog. The  $\text{O}_3$  concentration was also relatively high. The tetroon drifted slowly toward San Francisco and passed over the shoreline at 1037.

The tetroon was over the land between 1037 and 1056. During this interval it rose several hundred feet but was never more than 200 meters from the shoreline. Because the computer failed between 1105 and 1130, no data are available for this interval. However, the 5-minute average at 1102 (30 minutes elapsed time) is the pollutant concentration measured immediately after the houseboat resumed track-

ing of the tetroon. The NO and NO<sub>2</sub> concentrations increased and the O<sub>3</sub> concentration decreased while the air mass was over San Francisco.

The tetroon was tracked until it descended to the houseboat at 1235. If the tetroon had not descended, it probably could have been tracked for 1 to 2 more hours. During this interval, both photochemical activity and dilutional effects were observed.

There was a data acquisition system failure between 1105 and 1130, probably due to the decrease in the voltage output of the batteries used to power the computer. When the computer was started again, the concentration of NO was observed to be very high. As can be seen from the houseboat course (Figure 3), the houseboat was just below the Pacific Gas and Electric (PG&E) power plant stacks at Hunters Point and Potrero Point and may have passed through their plumes. To examine this possibility in greater detail, a simple model was used to evaluate the importance of two large, point sources of oxides of nitrogen in the southeastern part of the city of San Francisco. These two power plants, about 3.1 kilometers apart, emit a total of about 15 tons per day of NO<sub>x</sub>.<sup>10</sup> The stacks at these plants are about 75 meters or less in height. To calculate concentrations, an equation was used to describe concentrations under conditions where diffusion proceeds fairly rapidly below an elevated inversion that prevents transfer of material to greater heights.<sup>11</sup>

The potential contribution of the power plants to the observed NO concentrations at 1040 on 21 September was estimated using wind speed and direction based on the observed trajectory of the tetroon. The path of the houseboat was generally along the periphery of the areas where the NO concentrations from the power plants were predicted to be a few parts per billion or less. At the center of these plumes, calculations indicated that NO concentrations could reach several tens of parts per billion. These calculated concentrations are based on hourly average concentrations.

The atmospheres below about 3000 meters was moderately unstable during the morning of 21 September, based on Turner's stability algorithm.<sup>12</sup> This unstable layer was capped by an inversion, hence, providing the necessary elements for "fumigation," and relatively large, short-term fluctuations of concentration. The period of high NO concentrations observed between 1134 and 1146 may have been caused by NO from the Potrero power plant. The plume from this plant may have penetrated the inversion layer at an earlier time and drifted over the area to the southeast with little lateral or vertical spreading; then as the lower parts of the inversion layer disintegrated, the relatively high concentrations may have been mixed to the surface by the motions in the moderately unstable air below. The increases in NO concentration are unaccompanied by comparable increases in the concentration of CO or CN, thereby indicating non-automotive pollution. Furthermore, the morning sounding at Oakland showed near calm winds within the inversion layer, a condition likely to cause the accumulation of relatively large pollutant concentrations within the layer. Admittedly, the above explanation cannot be fully documented, however, it appears to offer a reasonable explanation for the observations.

The aerosol particle counter (APC) data are summarized in Figure 6. Each point is  $dN/dr$ , which is the average number of particles per cubic centimeter per micron, measured during a 15-minute interval versus the particle size range for the channel. The lines connect counts for the same time period, as indicated by the average time adjacent to each line. The observation that there were equal number of particles in the 0.2-micron and 0.3-micron ranges was unexpected. Based on previous observations by SRI and other laboratories, the 0.2-micron particle count should be much larger than the 0.3-micron count. The dilutional effects can account for only about one-half of the dramatic decrease in the number of particles during the tetraon run. The remainder is probably due to evaporation of water from the particles.

This day was the first test of the houseboat mobile laboratory. Difficulties with the temperature sensor and the steady voltage decrease of the computer power supply resulted in the loss of valuable data. The highest smog levels for the entire sampling program were observed that day. It was also a day of ideal meteorological conditions; the air flow was southeasterly down the axis of the Bay at about 5 mph. If the tetroon had not descended to the surface because of a leak, the run would have been at least 4 hours instead of 2 hours. The high NO concentrations observed near Hunters Point were observed again on other days. On this particular day, the concentrations can be ascribed with near certainty to a portion of the Potrero PG&E power plant plume. On later days, the explanation is not as definitive. The experiment was highly successful in that it demonstrated that under meteorological conditions conducive to smog formation, valid pollutant concentration data can be obtained and the wind speeds and direction are such that long intervals of tetroon tracking are likely.

## 2. 25 October 1972

This sampling day was selected because a tetroon run was made in conjunction with airborne measurements of concentration gradients during an interval of photochemical activity. In addition, pollutant concentration mapping of the South Bay showed interesting evidence of pollutant inhomogeneities over the Bay.

Figures 7 through 12 are maps illustrating wind flow patterns, houseboat sampling paths, tetroon trajectories, rawinsonde observations, helicopter flight paths, pollutant concentrations, and aerosol particle data.

In the early morning, offshore breezes dominated the area. An easterly wind was established before 0800 and continued until about 1000. The onshore breeze was reestablished after 1000 and dominated the remainder of the day.

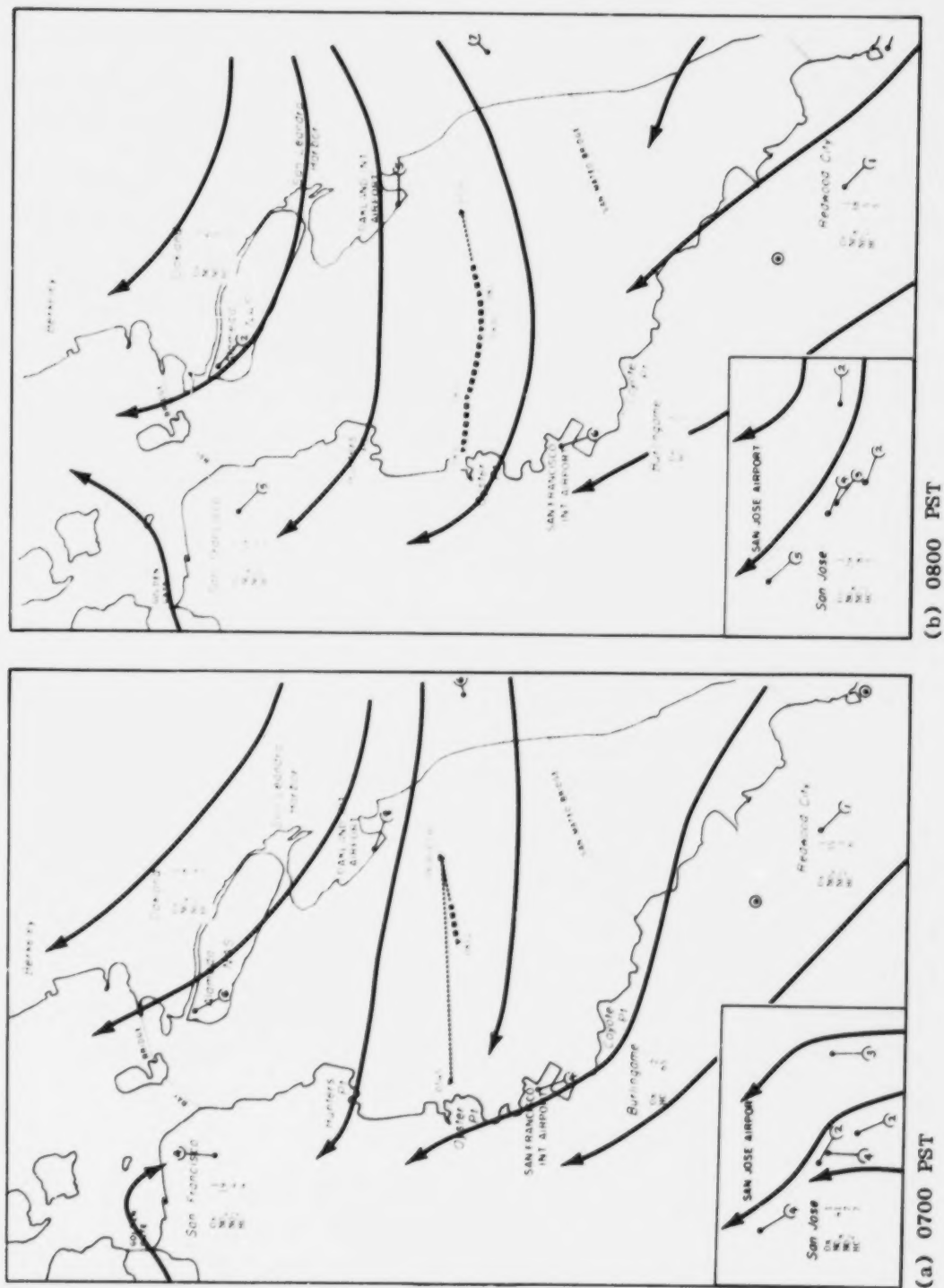
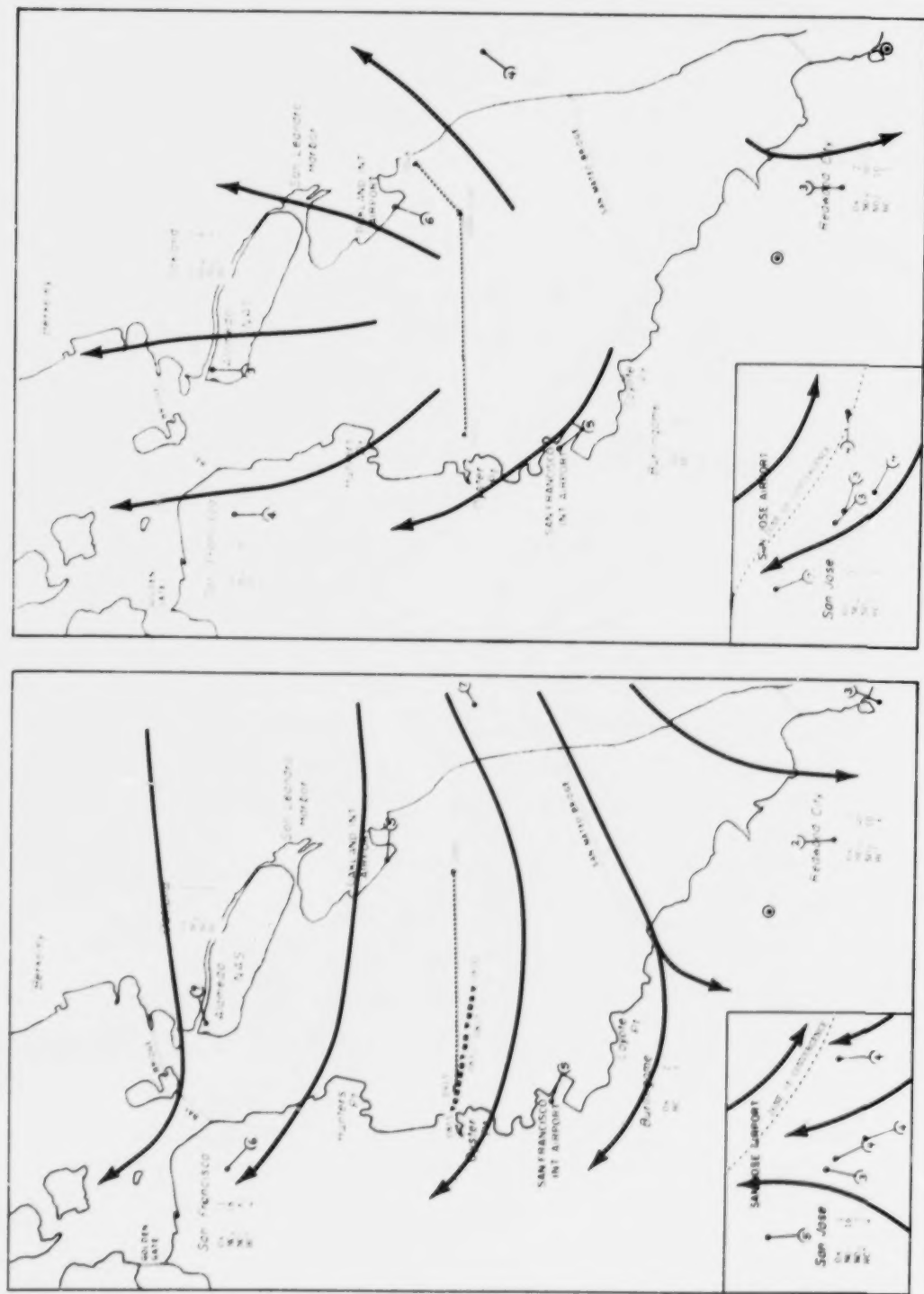


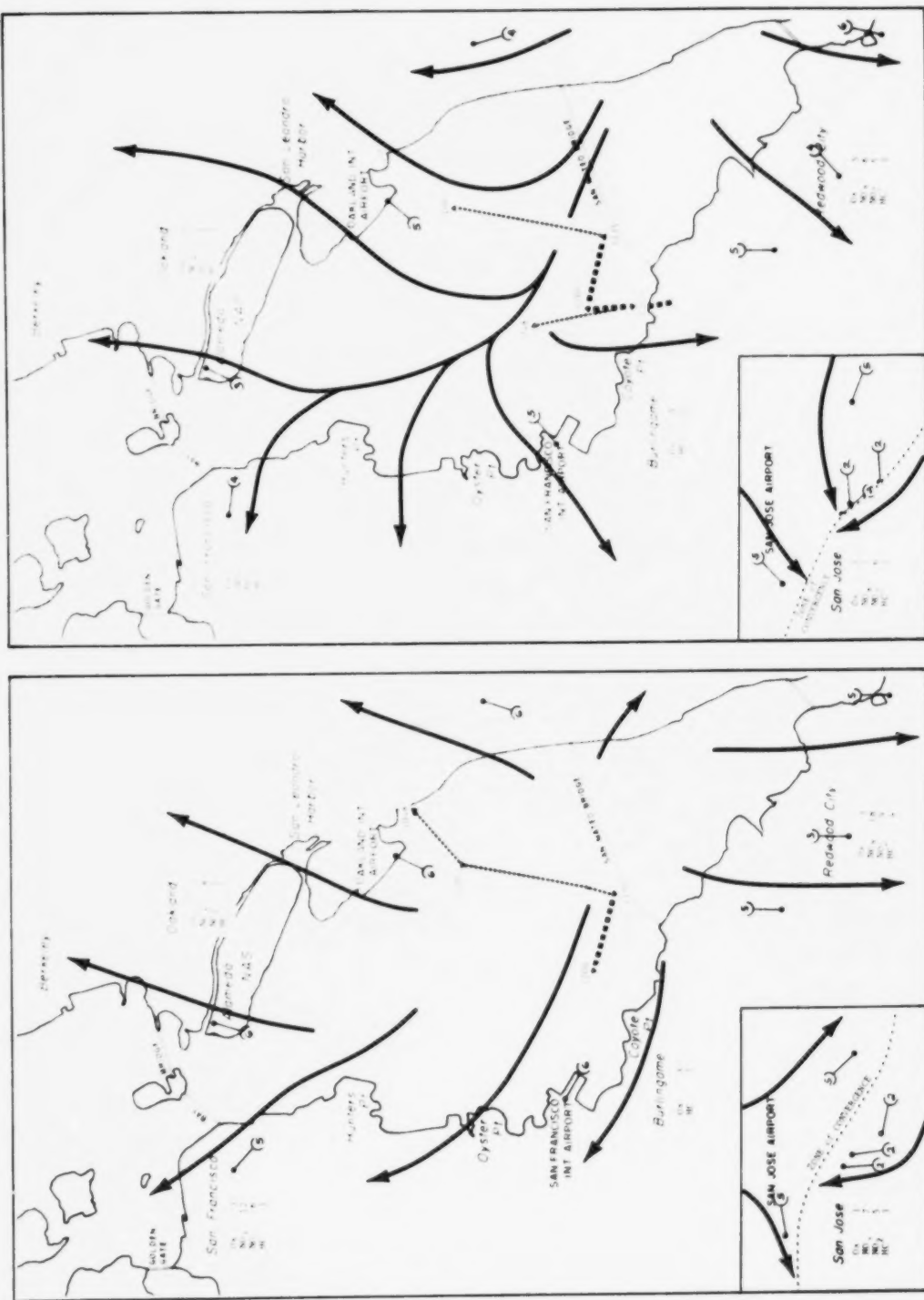
FIGURE 7 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 25 OCTOBER 1972



(c) 0900 PST

(d) 1000 PST

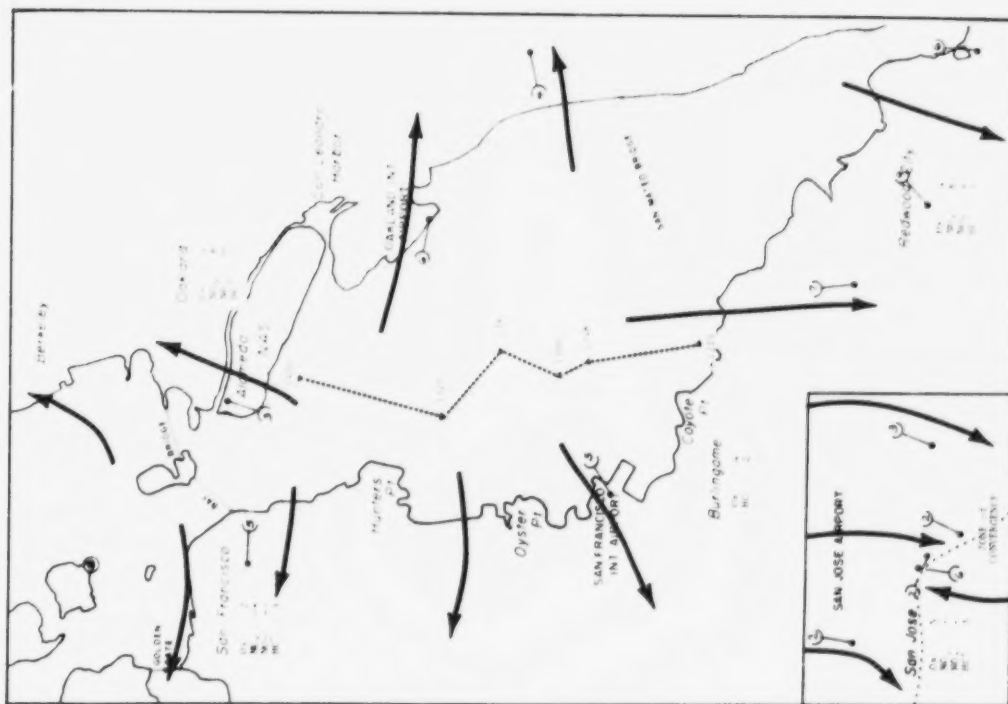
FIGURE 7 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 25 OCTOBER 1972 (Continued)



(e) 1100 PST

(f) 1200 PST

FIGURE 7 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 25 OCTOBER 1972 (Continued)



(g) 1300 PST

FIGURE 7 AIR POLLUTION LEVELS. SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 25 OCTOBER 1972 (Concluded)

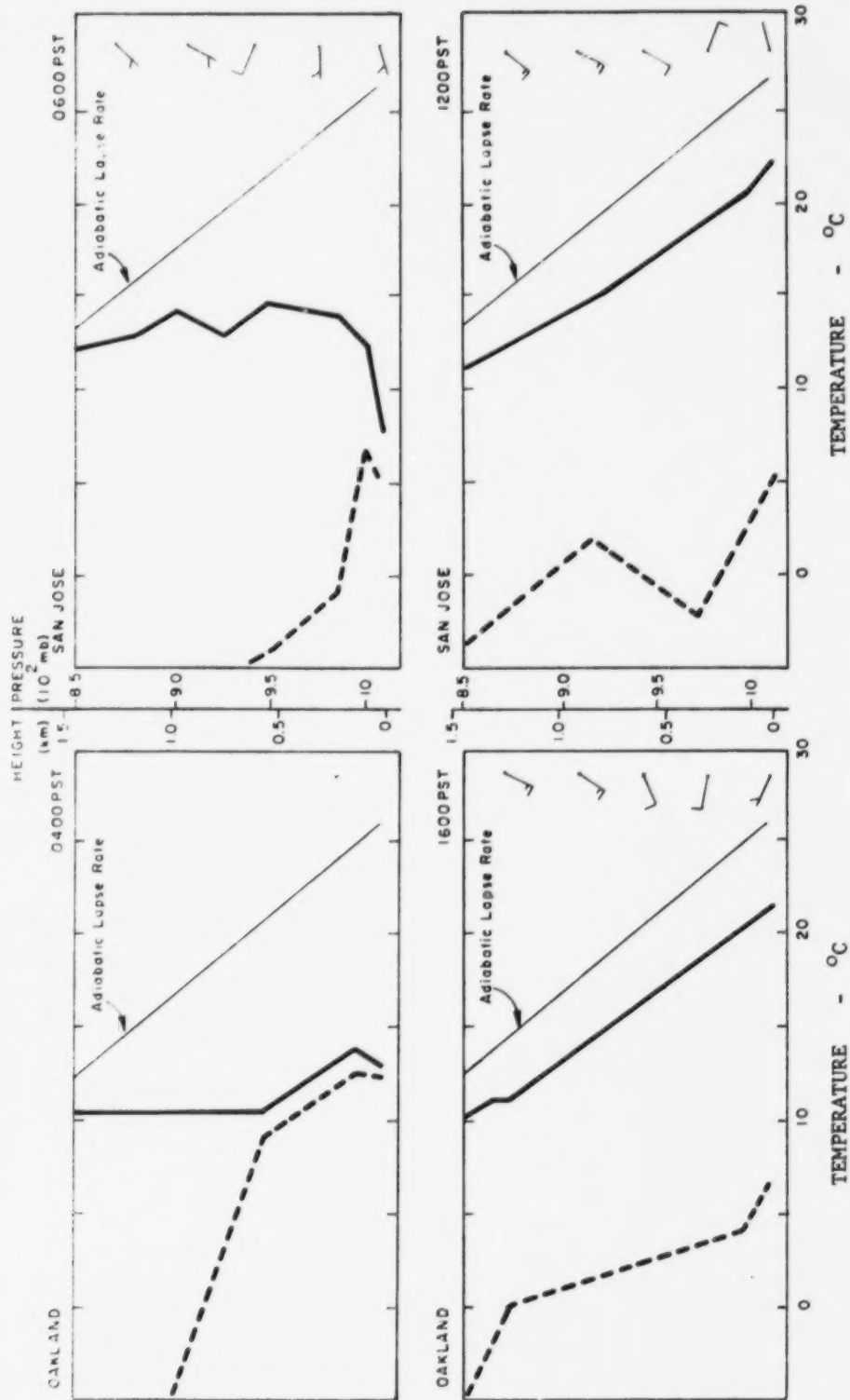


FIGURE 8 RAWINSONDE TEMPERATURE AND DEW POINT OBSERVATIONS, 25 OCTOBER 1972  
(Temperature —, Dew Point ----)

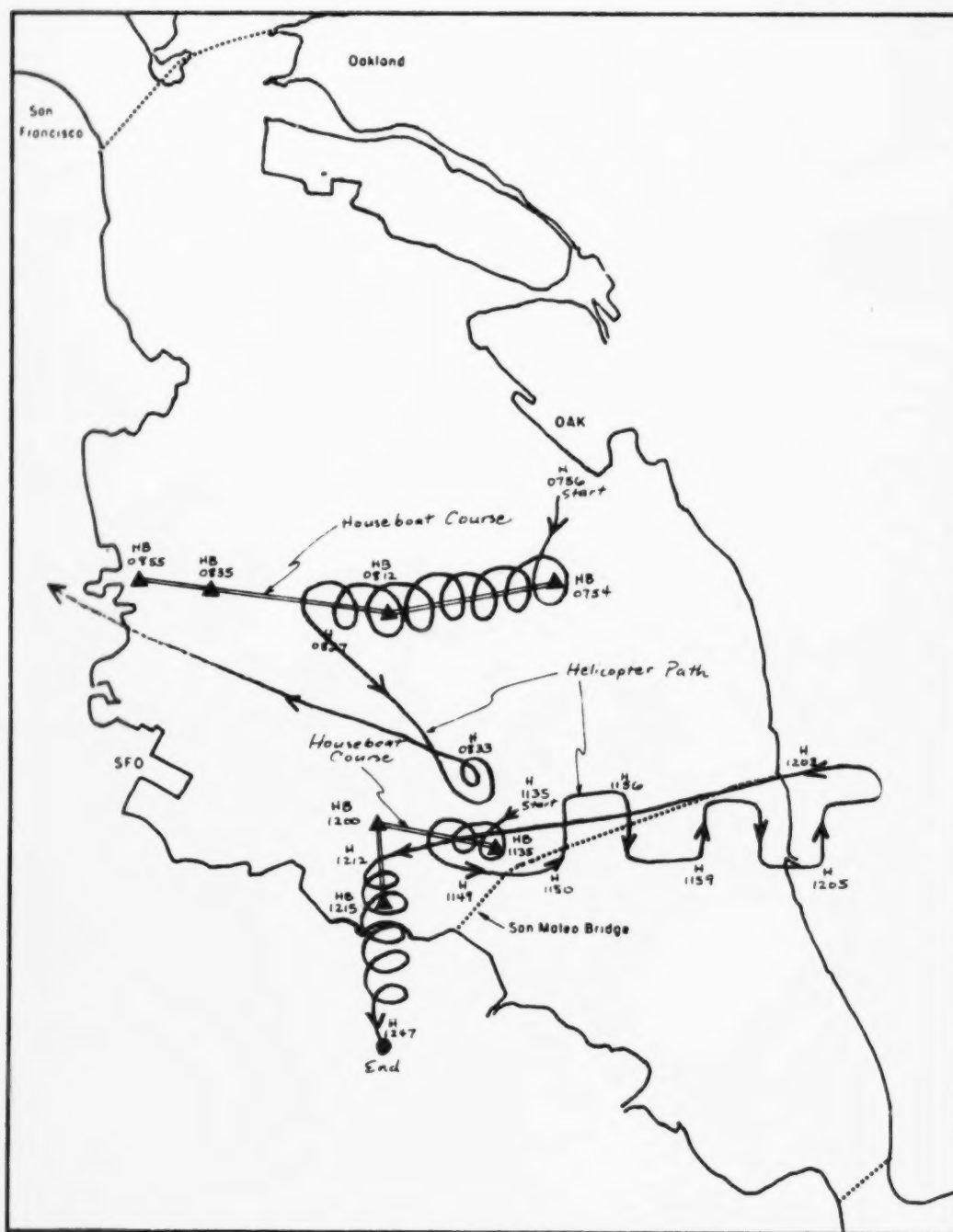


FIGURE 9 SAMPLING PATHS OF MOBILE LABORATORIES ON 25 OCTOBER 1972  
(HB - houseboat, H - helicopter)

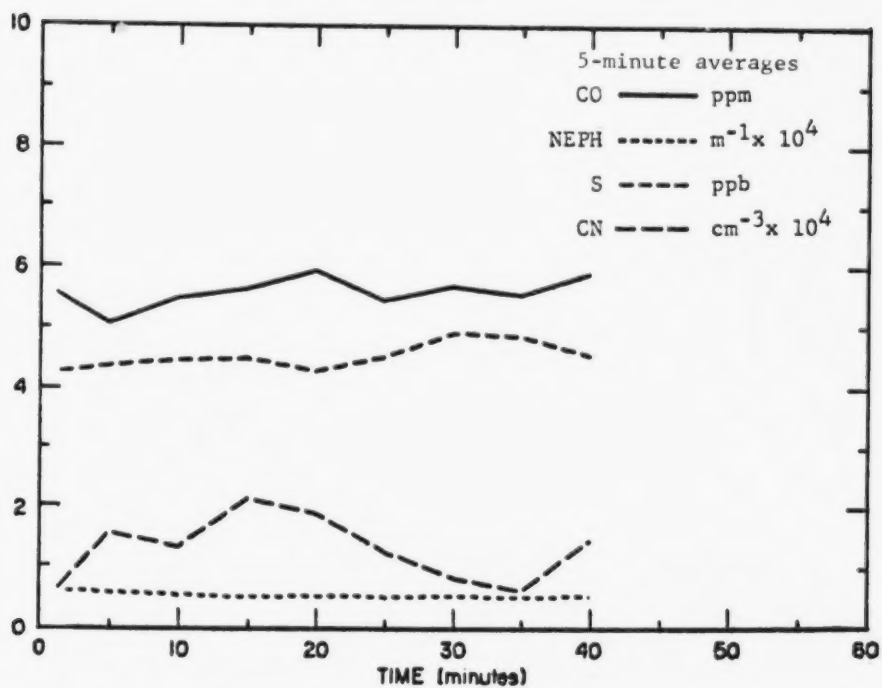
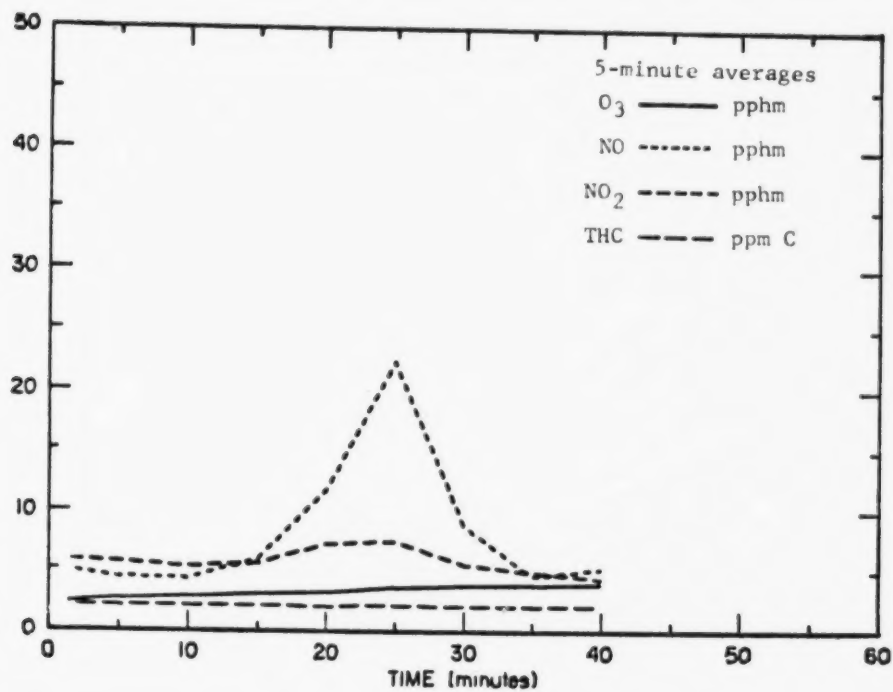
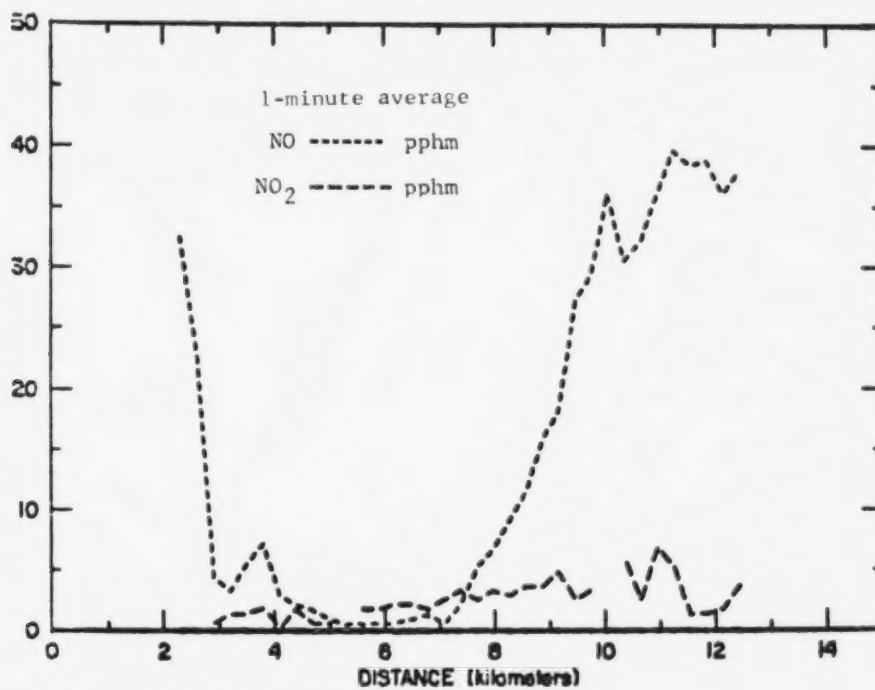
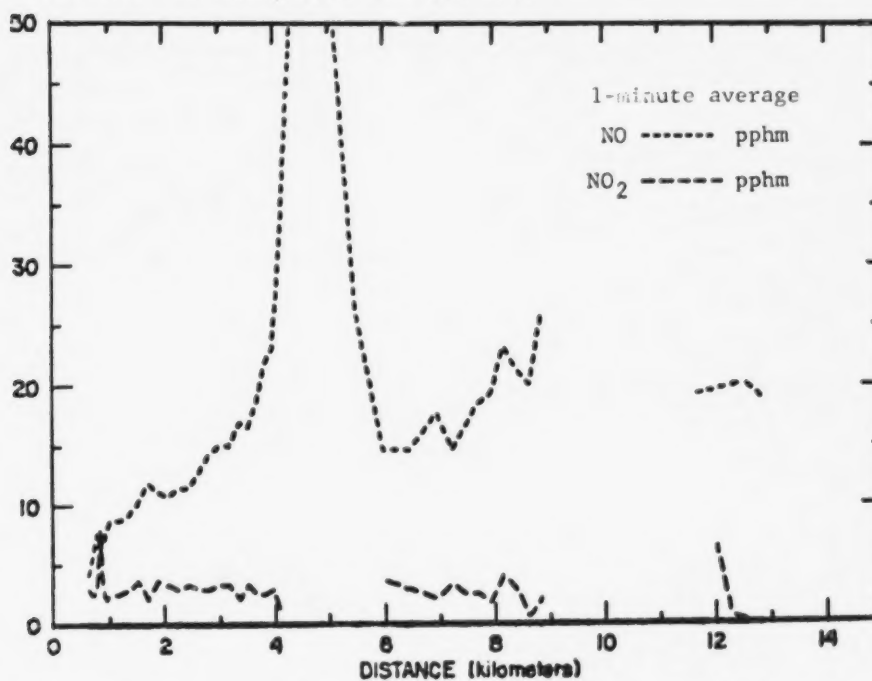


FIGURE 10 POLLUTANT CONCENTRATIONS OBSERVED DURING TETROON RUN,  
25 OCTOBER 1972, 1138 to 1218 PST

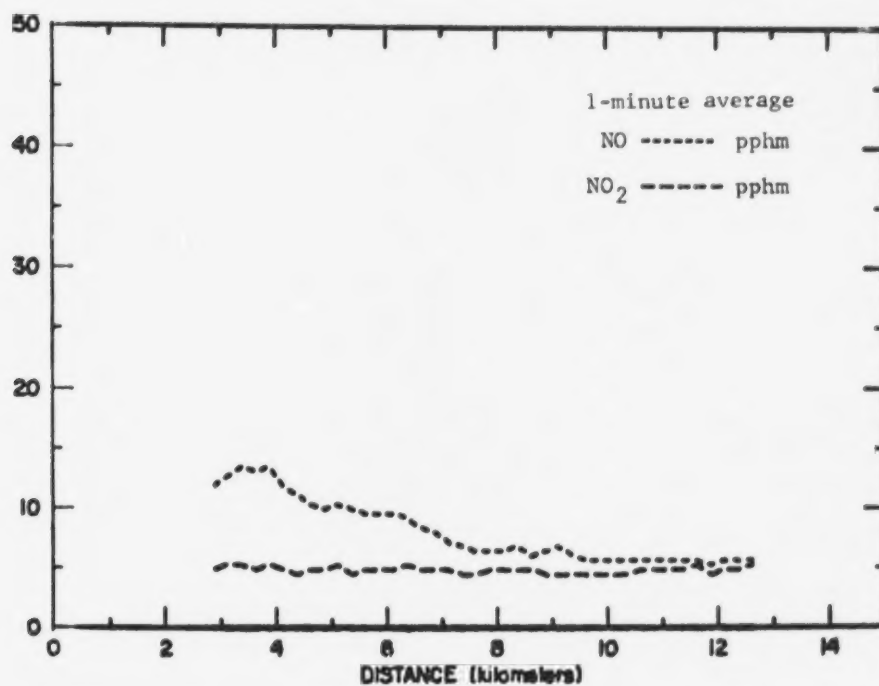


(a) WEST TO EAST, 0551 to 0625 PST



(b) EAST TO WEST, TRACKING TETROON, 0758 to 0855 PST

FIGURE 11 POLLUTANT MEASUREMENTS DURING TRAVERSES OF THE BAY,  
 25 OCTOBER 1972



(c) WEST TO EAST, 0916 to 0955 PST  
FIGURE 11 POLLUTANT MEASUREMENTS DURING TRAVERSES OF THE BAY,  
25 OCTOBER 1972 (Concluded)

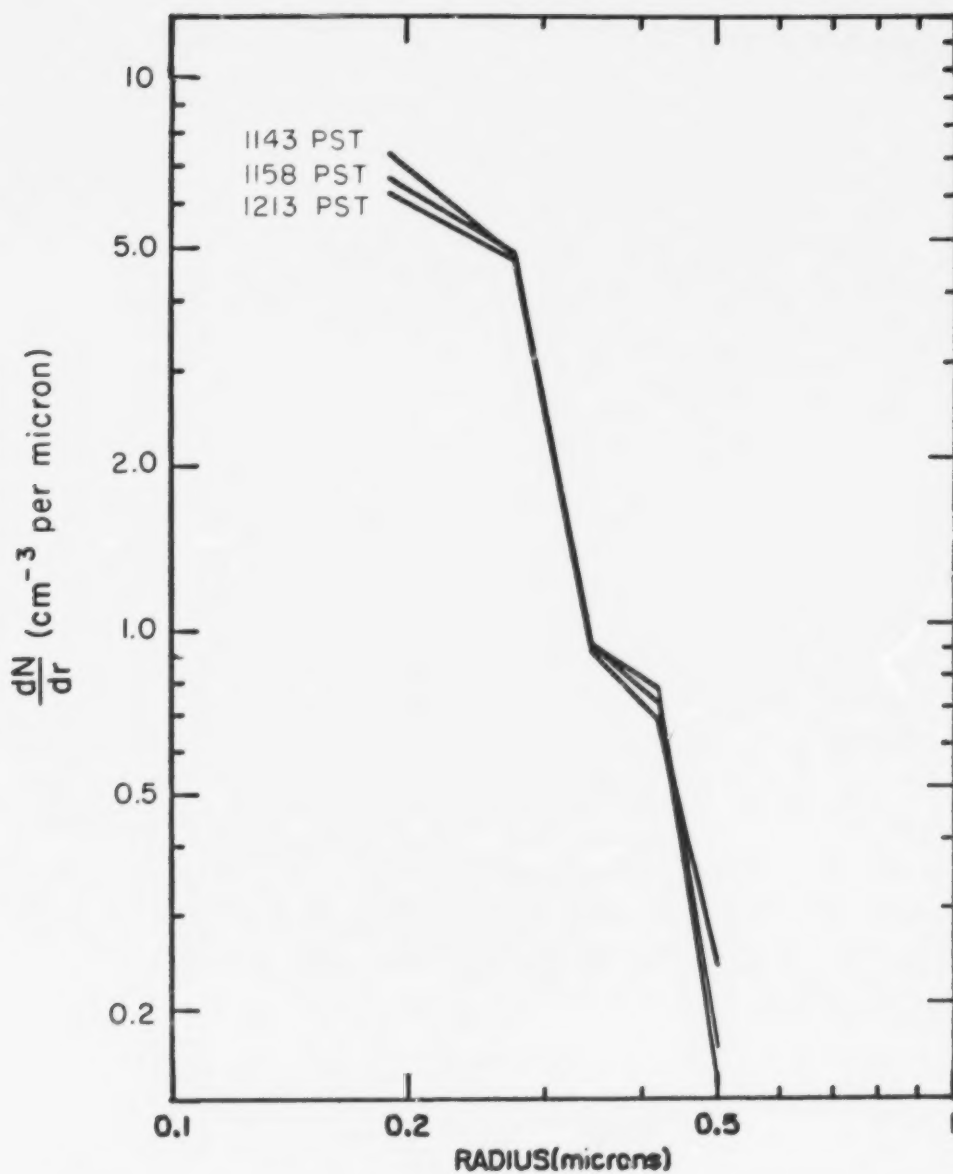


FIGURE 12 AEROSOL PARTICLE COUNTER DATA FOR VARIOUS AVERAGE TIMES,  
25 OCTOBER 1972, 1143 to 1226 PST

The rawinsonde data, shown in Figure 8, indicate that a shallow inversion (90 meters) was observed at Oakland Airport at 0400. The helicopter soundings measured from 0831 to 0849 indicate that the atmosphere was relatively stable at the lower altitudes and that the soundings more nearly resembled those obtained at San Jose from the 0600 rawinsonde than those from Oakland.

Two tetroon runs were made on 25 October, the first 0756 to 0857, and the second 1135 to 1220. The first run was not analyzed since complete air quality data were not available due to instrument malfunctions. The path of the second tetroon run is shown in Figure 7. The tetroon, released near the San Mateo Bridge, drifted west until a period of stagnation occurred at 1156 that lasted until 1208. When the tetroon began moving again, the wind direction had shifted, causing the tetroon to move southward as shown in Figure 7(f). During the period of stagnation, the tetroon continued to move at slow speeds with erratic direction of flight. Contamination by the exhaust gases of the houseboat was unavoidable during this interval.

The plots of pollutant concentrations versus time are shown in Figure 10 for  $O_3$ , NO,  $NO_2$ , and THC. The  $O_3$  plot indicates a concentration increase during the sampling run, though it must be emphasized that the observed  $O_3$  concentration was not substantially above background levels. The  $O_3$  concentration increased from 2.4 pphm to 4.0 pphm during the 45-minute interval of the tetroon run. The increase in  $O_3$  during this sample run indicates that photochemistry had taken place. The THC concentration decreased during this interval from 2.2 ppm C to 2.0 ppm C. This reduction in THC, though not large, is greater than experimental error.

A plot of total S, nephelometer, CN, and CO is shown in Figure 10. The concentration of CO remains relatively constant throughout the tetroon run, indicating that the marked air parcel was undergoing dilution with adjacent air parcels containing similar concentrations of CO as the marked parcel rather than unpolluted air. The total sulfur concentration increased during the tetroon run from 8.5 ppb to 9.7 ppb. This could be attributed to presence of shallow water with decomposition of organics on the mud floor of the Bay.

The CN count varied considerably on a short term basis throughout the tetroon run. A corresponding increase in NO that would substantiate exhaust gas contamination was not observed until stagnation. The NO to NO<sub>2</sub> ratio indicates the presence of well-aged smog even though the sample run was started downwind of the San Mateo Bridge. The source of pollutants is probably auto exhaust from the East Bay or the South Bay. The emissions from automobiles on the San Mateo Bridge did not significantly alter the pollutant mixture. During the tetroon run, pollutant measurements were made by the helicopter to determine concentration gradients. Table 4 is a comparison of houseboat measurements with the helicopter measurements. The concentration gradient measurements made by the helicopter from 1148 to 1210 are not included in Table 4. The helicopter continued to track the tetroon after houseboat tracking was terminated.

The helicopter measurements correlate reasonably well with the concentrations observed on the houseboat (except for NO<sub>x</sub> concentrations at 1142 and 1148). Vertical and horizontal pollutant concentration gradients were small. The measurements from the helicopter indicate that the pollutant concentrations decreased until near background levels were reached after the houseboat terminated the run.

Table 4  
DATA FOR 25 OCTOBER 1972, 1137 TO 1258 PST  
(1-Minute Averages)

| Houseboat |              |                           |                          |              | Helicopter |             |              |                           |                          |              |
|-----------|--------------|---------------------------|--------------------------|--------------|------------|-------------|--------------|---------------------------|--------------------------|--------------|
| Time      | NO<br>(pphm) | NO <sub>x</sub><br>(pphm) | O <sub>3</sub><br>(pphm) | Temp<br>(°C) | Time       | Alt<br>(ft) | NO<br>(pphm) | NO <sub>x</sub><br>(pphm) | O <sub>x</sub><br>(pphm) | Temp<br>(°C) |
| 1137      | 5.6          | 11.9                      | 2.3                      |              | 1137       | 200         | 4.8          | 9.6                       | 1.8                      | 24.2         |
| 1140      | 5.3          | 11.9                      | 2.3                      |              | 1140       | 300         | 5.0          | 10.0                      | 1.7                      | 24.2         |
| 1142      | 4.5          | 11.6                      | 2.7                      |              | 1142       | 350         | 2.4          | 4.8                       | 2.0                      | 24.2         |
| 1148      | 4.9          | 10.7                      | 2.7                      |              | 1148       | 500         | 1.2          | 4.8                       | 1.8                      | 24.2         |
| 1210      | 6.8          | 13                        | 3.9                      | 24.4         | 1210       | 500         | 4.8          | 7.2                       | 2.2                      | 24.4         |
| 1212      | 6.4          | 12.3                      | 3.5                      | 24.1         | 1212       | 500         | 7.2          | 9.6                       |                          | 24.4         |
| 1215      | 2.9          | 8.9                       | 3.9                      | 23.8         | 1215       | 500         | 3.6          | 3.6                       | 2.8                      | 24.4         |
|           |              |                           |                          |              | 1225       | 500         | 1.5          | 7.0                       | 3.2                      | 24.3         |
|           |              |                           |                          |              | 1230       | 500         | 1.0          | 1.5                       | 2.2                      | 24.3         |
|           |              |                           |                          |              | 1235       |             | 1.0          | 1.5                       | 1.8                      | 24.3         |
|           |              |                           |                          |              | 1240       |             | 1.0          | 2.0                       | 1.7                      | 24.3         |
|           |              |                           |                          |              | 1245       |             | 1.0          | 2.0                       | 2.0                      | 24.4         |
|           |              |                           |                          |              | 1258       |             | 1.5          | 2.5                       | 2.0                      | 24.4         |

On 25 October the inhomogeneous distribution of NO concentrations over the Bay was observed. Three traverses across the Bay between Oyster Point and San Leandro Harbor were made over nearly identical paths: the first, west to east 0545 to 0627; the second, a tetroom run, east to west 0756 to 0857; and the third, west to east at 0916 to 0955. The concentration of NO and NO<sub>2</sub> for these traverses was plotted as a function of distance, as shown in Figure 11. The NO<sub>2</sub>, CO, THC, and O<sub>3</sub> concentrations did not vary appreciably during these traverses, except during the interval of the exhaust gas contamination at 5 kilometers from the western shore, as shown in Figure 11(b). However, large variations in

NO concentrations were observed during all traverses. During the first traverse the low concentrations of NO at the center of the Bay are probably the result of limited encroachment of polluted air from the shore during the early morning offshore breezes. The NO concentration plots for the second and third traverses indicate that the air mass containing high NO concentration advected toward the western shore of the Bay.

From 1220 to 1255 on 25 October, we again observed the inhomogeneity of NO concentrations over the Bay. Over a distance of about 5 kilometers, the NO concentration changed, on the basis of 5-minute averages, from 5.2 pphm to nearly 40 pphm and then decreased to 6.7 pphm. During this interval the changes in other pollutants, on a 5-minute average basis, were  $\text{CO} = 5.4 \text{ ppm} \pm 0.5 \text{ ppm}$ ,  $\text{THC} = 1.9 \text{ ppm C} \pm 0.1 \text{ ppm C}$ ,  $\text{O}_3 = 4.7 \text{ pphm} \pm 0.7 \text{ pphm}$ ,  $\text{CN} = 15.1 \times 10 \text{ cm}^{-3} \pm 5.0 \times 10 \text{ cm}^{-3}$ , and  $\text{NO}_2 = 6.0 \text{ pphm} \pm 2.6 \text{ pphm}$  (Appendix E, Table E-10). On the basis of meteorological observation from shore stations and the houseboat, this "pocket" of high NO concentrations could not be attributed to the emissions from the power plants located at Potrero Point and Hunters Point.

Particulate data were also collected on 25 October. The APC data are summarized in Figure 12; Table 5 is the chemical analyses of the particulate matter collected on a high-volume filter. In contrast to the APC data for 21 September, the particle size distribution did not change with time during the tetraon run on 25 October. However, the meteorological conditions were very different, since hot, dry air from the southeast was blowing across the Bay. On the other hand, the chemical analysis of the collected particulate is similar to that collected on 2 November and 6 November (see Section V.B.4 and Appendix C for complete data).

Table 5

CHEMICAL ANALYSIS OF PARTICULATE MATTER COLLECTED  
ON GLASS FIBER FILTERS, 25 OCTOBER 1972

| Time (PST) | Mass Loading<br>( $\mu\text{g}/\text{m}^3$ ) | Chemical Composition ( $\mu\text{g}/\text{m}^3$ ) |        |          |      |
|------------|----------------------------------------------|---------------------------------------------------|--------|----------|------|
|            |                                              | Nitrate                                           | Sulfur | Chloride | Lead |
| 0800-1104  | 108                                          | 9.6                                               | 3.7    | 2.5      | 2.7  |
| 1235-1320  |                                              |                                                   |        |          |      |

3. 26 October 1972

This date was selected to document the observed inhomogeneities of pollutant concentrations immediately downwind of San Francisco. A tetron run without evidence of photochemical activity was analyzed to describe the complex dispersion and dilutional processes observed over the Bay. In addition an area of high NO concentration was observed that can be at least partially attributed to power generating plants south of San Francisco.

Figures 13 through 15 are maps illustrating wind flow patterns, houseboat sampling paths, tetron trajectories, rawinsonde observations, and pollutant concentrations.

The winds were west to southwest throughout the sampling day. The stratus layer was overcast to broken throughout the sampling interval. The rawinsonde observations shown in Figure 14 indicate that a surface based shallow inversion (90 meters) was observed at Oakland Airport at 0400.

A tetron run was made on 26 October from 0907 to 0947. The trajectory of the tetron and the houseboat path are shown in Figure 13. The tetron was launched immediately downwind of San Francisco and drifted over Treasure Island. The houseboat temporarily abandoned



(b) 0800 PST

(a) 0700 PST

FIGURE 13 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 26 OCTOBER 1972

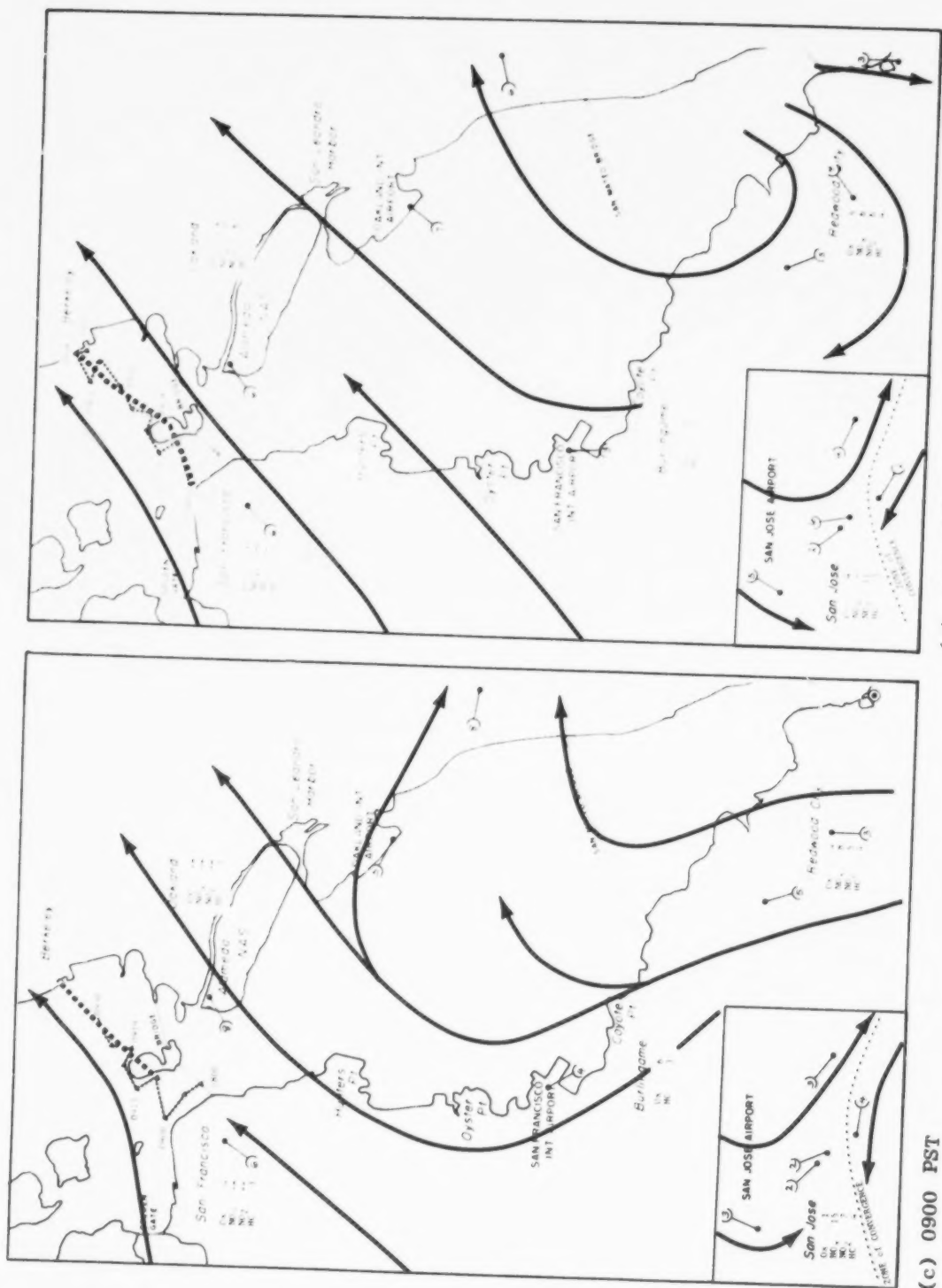


FIGURE 13 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 26 OCTOBER 1972 (Concluded)

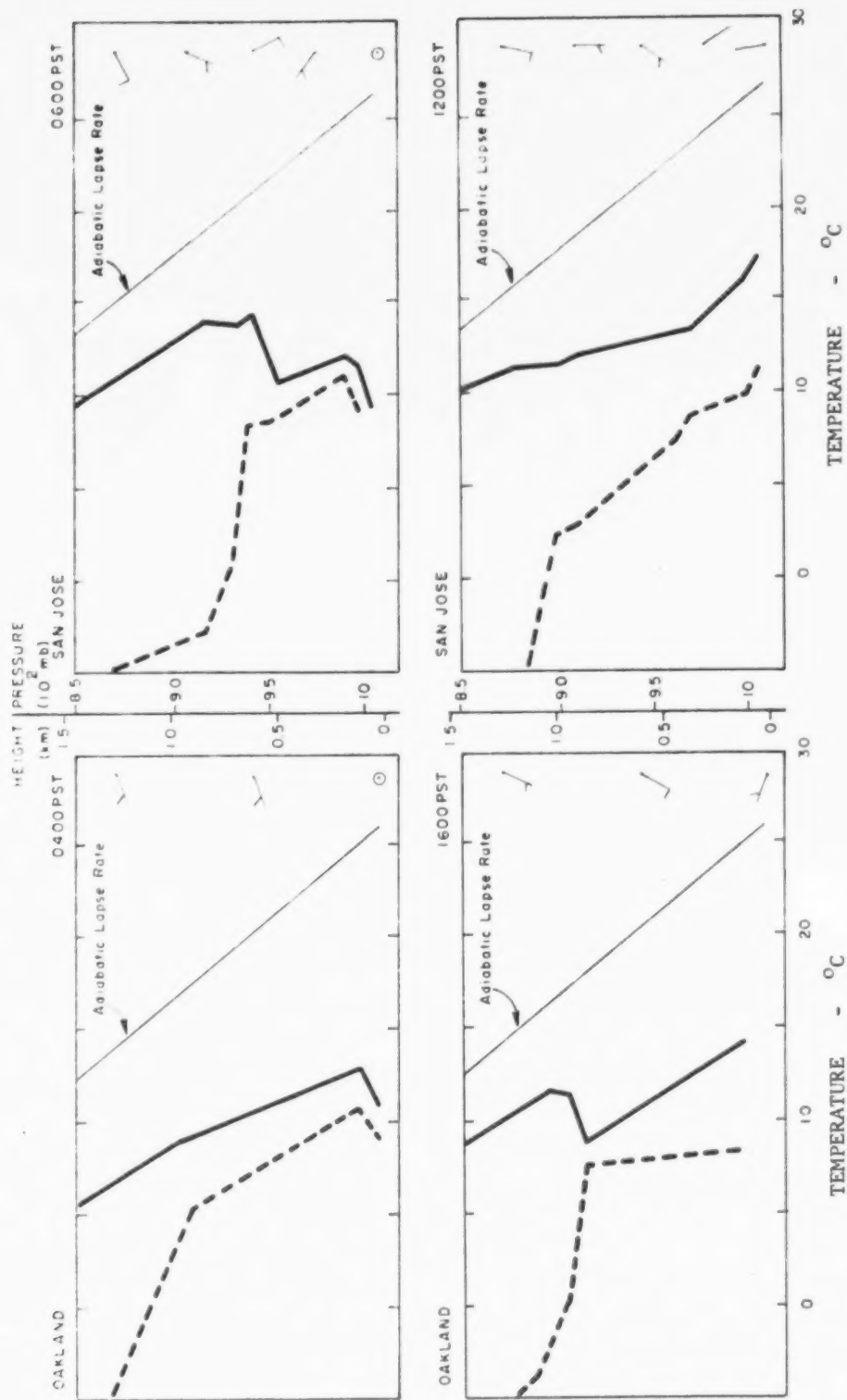


FIGURE 14 RAWINSONDE TEMPERATURE AND DEW POINT OBSERVATIONS, 26 OCTOBER 1972  
(Temperature —, Dew Point ----)

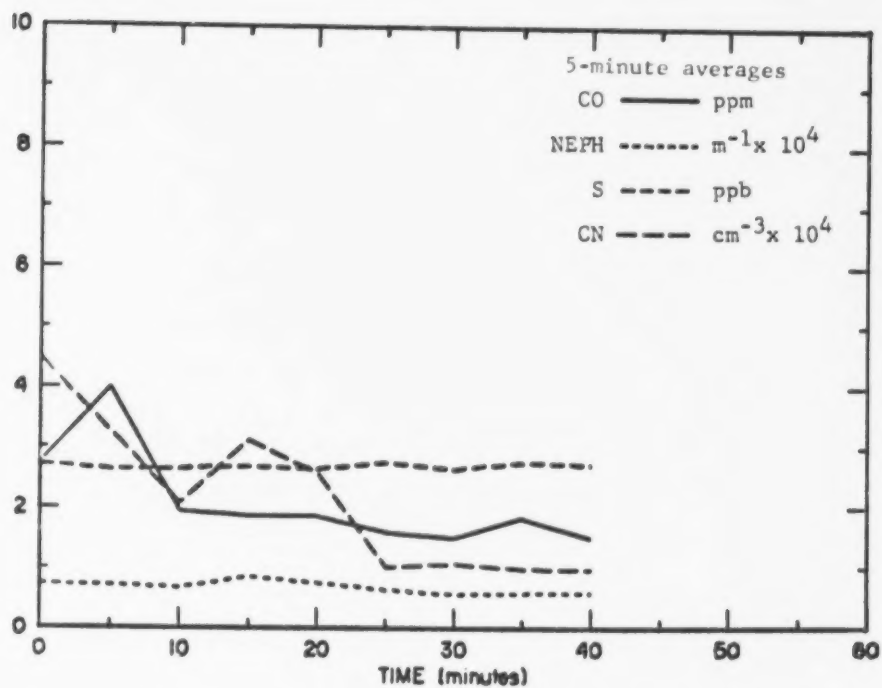
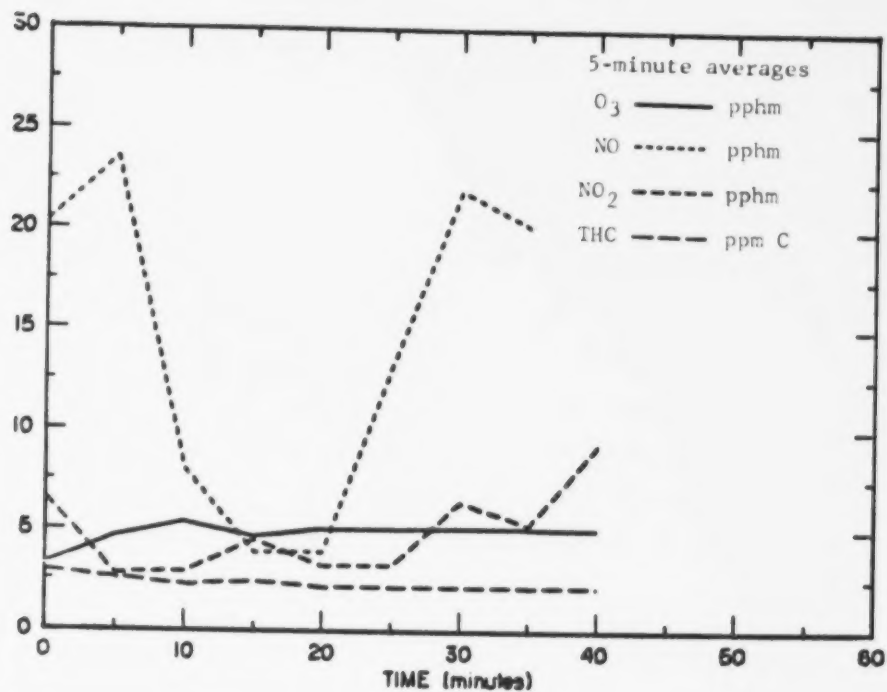


FIGURE 15 POLLUTANT CONCENTRATIONS OBSERVED DURING TETROON RUN, 26 OCTOBER 1972, 0907 to 0947 PST

the tetroon at Treasure Island, resumed tracking beyond Treasure Island at 0919, and followed the tetroon to the Berkeley shore.

The graphs displaying the changes in pollutant concentrations versus time during the tetroon run are shown in Figure 15. Extreme spatial and temporal variability were observed in the concentration of pollutants, particularly NO, within 1 kilometer downwind of San Francisco. Due to the multiplicity of sources in the city, the air mass was not well mixed for appreciable distances downwind of a large urban source. The high NO to NO<sub>2</sub> concentrations at the beginning of the tetroon run indicate that auto emissions from San Francisco are the primary source of pollutants. A rapid decrease in the concentration of NO occurred during the initial 15 minutes of the tetroon run. The concentration of other pollutants did not decrease so dramatically during this interval. The marked decrease in NO concentrations relative to other pollutants indicates that dilution occurs by air containing a variable mixture of pollutants after passage over the urban source or that the houseboat is overrunning surface air containing a well-aged pollutant burden. Dilution by clean marine air, on the other hand, would have significantly reduced in similar proportions the concentration of all pollutants. The low pollutant concentrations observed immediately downwind of Treasure Island when tracking was resumed at 0919 remained at low levels until 0931, after which NO and NO<sub>2</sub> concentrations abruptly increased. No corresponding increase in CO, THC, or CN occurred during this later portion of the tetroon run. This pollutant mixture is characteristic of some types of nonautomotive pollution such as power plants. Two

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\* Estimates of pollutant concentration variability near shore may be found in Table E-12. The variability of pollutant concentration in well-mixed air parcels did not normally exceed  $\pm 10\%$  except on those occasions where NO concentrations were very high. Based on dilution alone (see Figure 15), a rough estimate of the distance required to attain well mixedness is 2 to 4 kilometers downwind of the source. A determination of the well-mixedness as a function of meteorological conditions and source distance could be made by statistical analysis of the data.

power plants are located upwind at Hunters Point and Potrero Point and their plumes could conceivably have reached the houseboat under the meteorological conditions of this day. However, calculations with the model discussed earlier predict increases in NO concentrations of only 1 or 2 pphm, much less than those observed. The 12 to 13 kilometer distance between the houseboat and the power plants would result in plumes being reasonably well mixed and therefore, concentration fluctuations should be small.<sup>11</sup> Other sources, such as San Francisco, Treasure Island, or the Bay Bridge could have contributed to the observed atmospheric burden, but the BAAPCD lists no other major, individual sources of NO in the proper location that are comparable to the two power plants.

Although the sample run on 26 October did not indicate that significant photochemistry was taking place within the air mass, the run was indicative of the complex dilutional processes present over the Bay. In addition, this sample run indicates that the contribution from sources relatively far removed from the trajectory of the tetroon must be considered in interpreting the observed pollutant measurements.

#### 4. 2 November 1972

The meteorological conditions on this day, as on September 21, were almost ideal. The pollutant levels were lower than September 21, but photochemistry definitely occurred during the tetroon run of almost 2 hours. Figures 16 through 19 are maps illustrating wind flow patterns, houseboat sampling paths, tetroon trajectories, rawinsonde observations, and pollutant concentrations. The chemical analyses of Lundgren impactor samples reported by AIHL\* are summarized in Appendix F.

The morning soundings for Oakland and San Jose both show a very shallow surface inversion of about 0.1 kilometer thickness. At San Jose, a second inversion is present between 0.3 and 0.5 kilometers.

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\*Air and Industrial Hygiene Laboratory, Berkeley, California

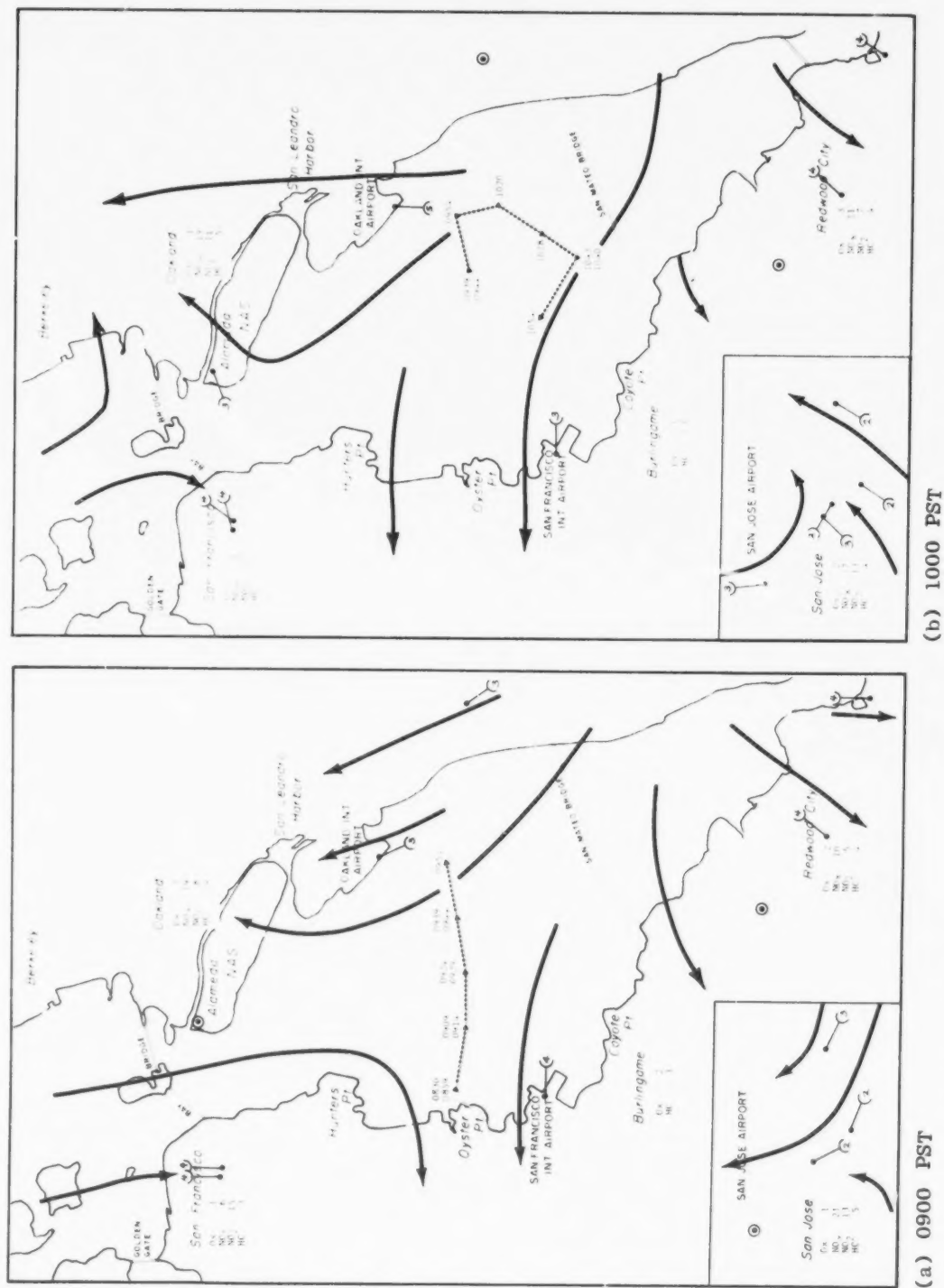
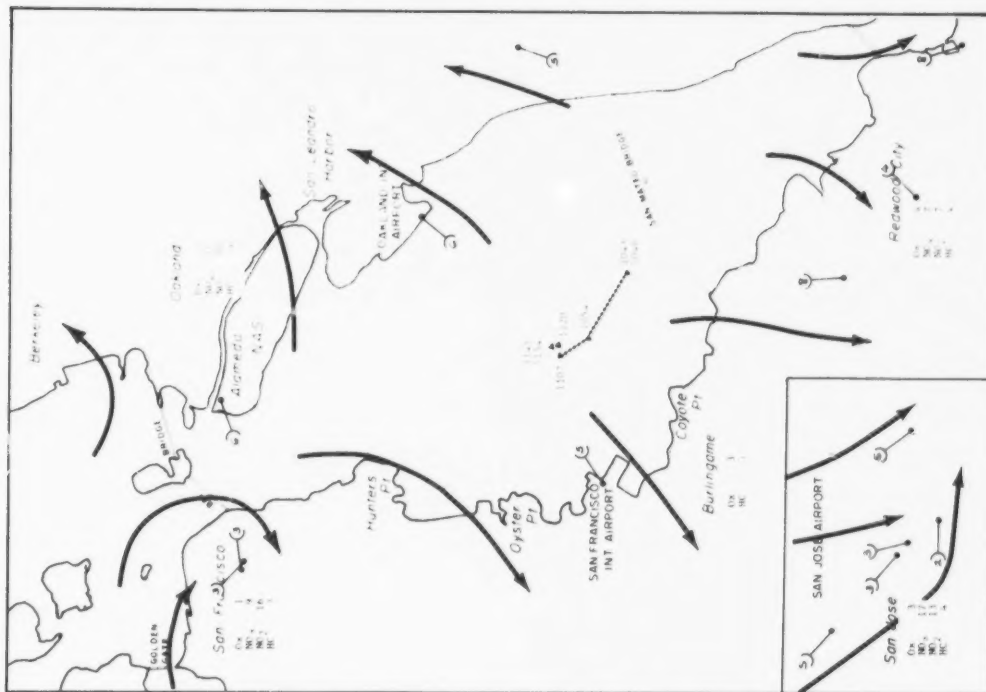
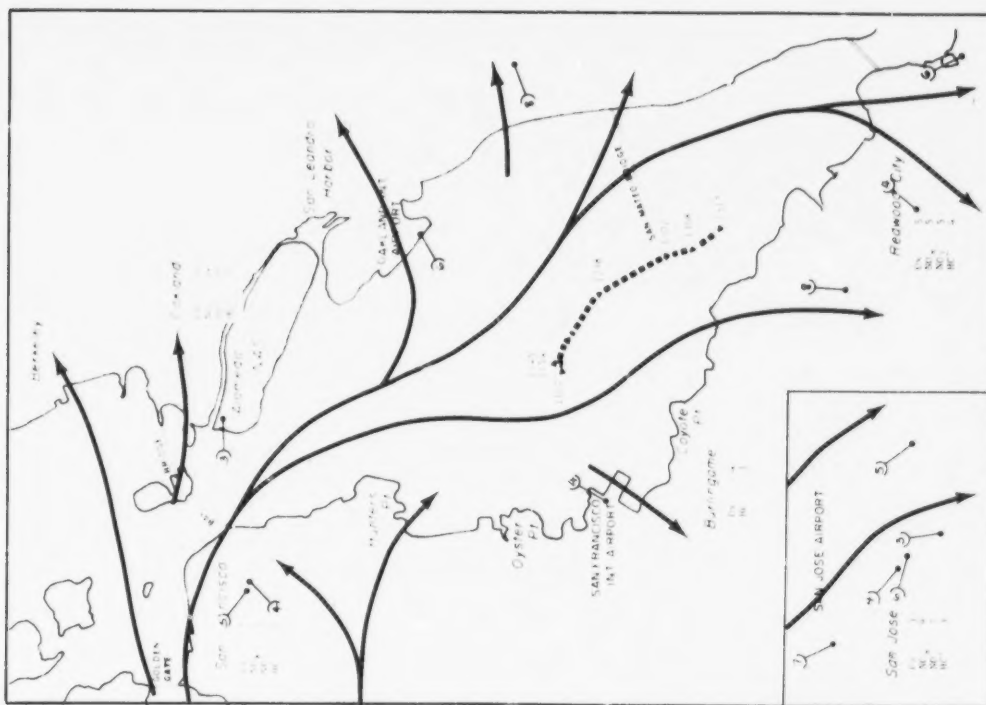


FIGURE 16 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 2 NOVEMBER 1972

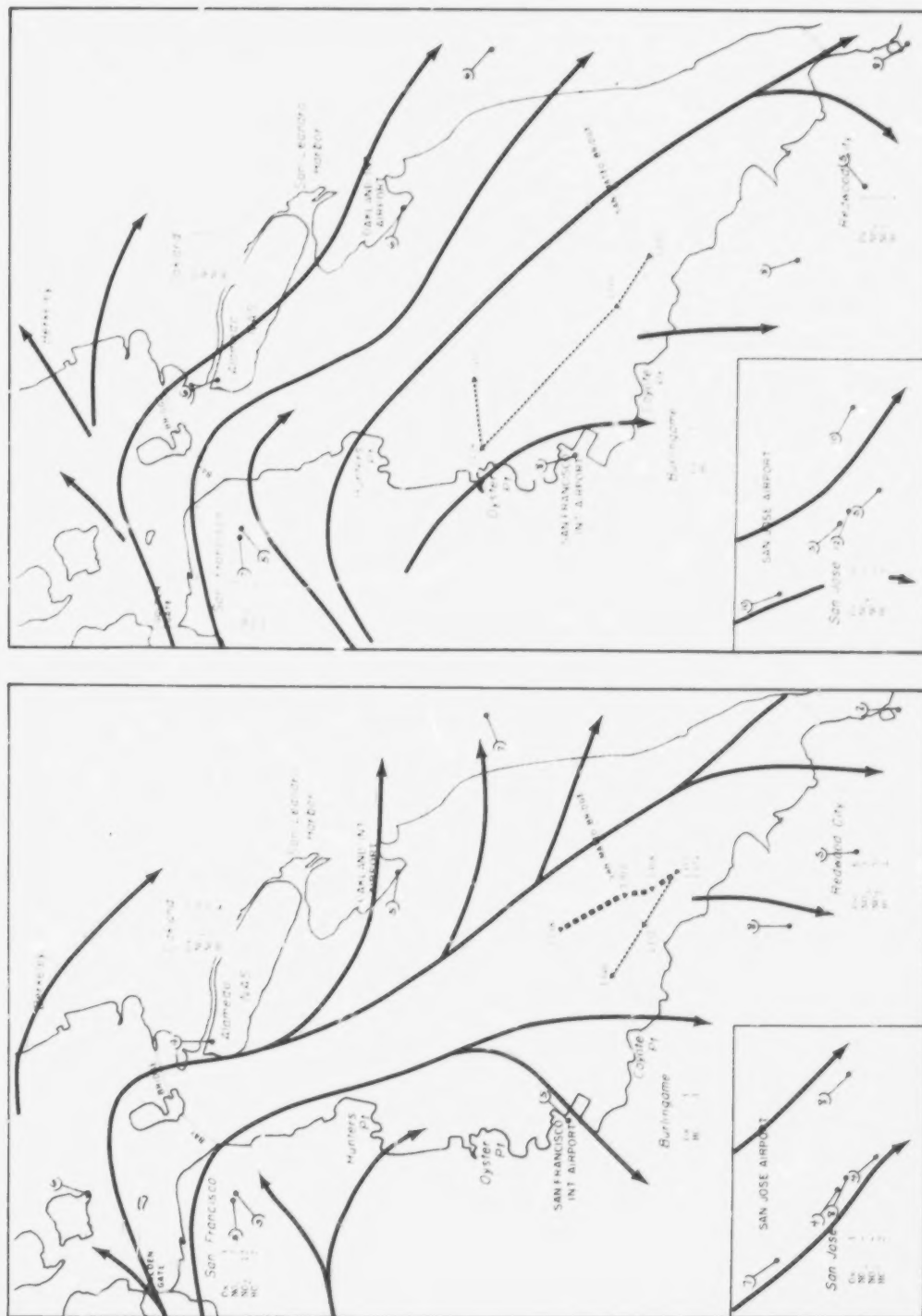


(c) 1100 PST



(d) 1200 PST

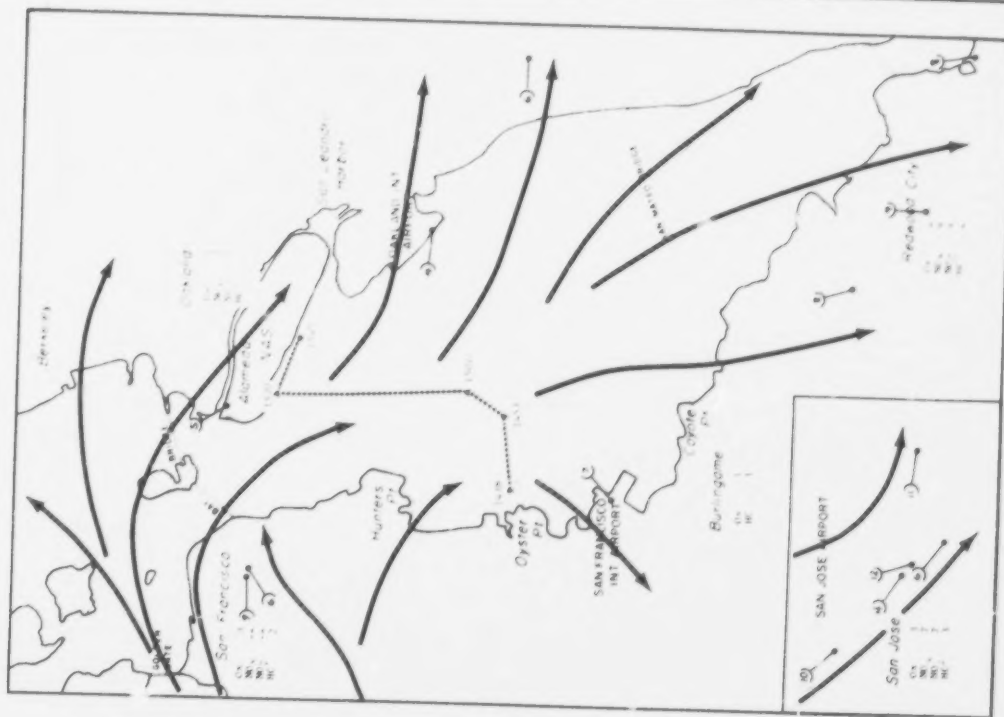
FIGURE 16 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 2 NOVEMBER 1972 (Continued)



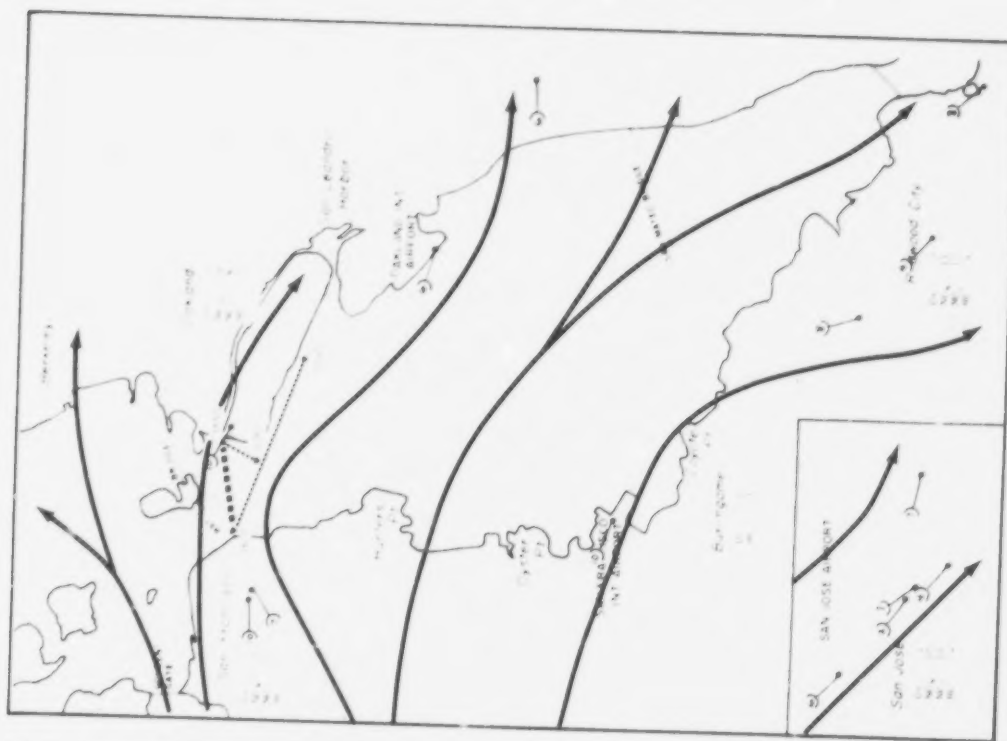
(f) 1400 PST

(e) 1300 PST

FIGURE 16 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 2 NOVEMBER 1972 (Continued)



(g) 1500 PST



(h) 1600 PST

FIGURE 16 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 2 NOVEMBER 1972 (Continued)



(i) 1700 PST

FIGURE 16 AIR POLLUTION LEVELS, SURFACE WIND FLOW, AND HOUSEBOAT COURSE, 2 NOVEMBER 1972 (Concluded)

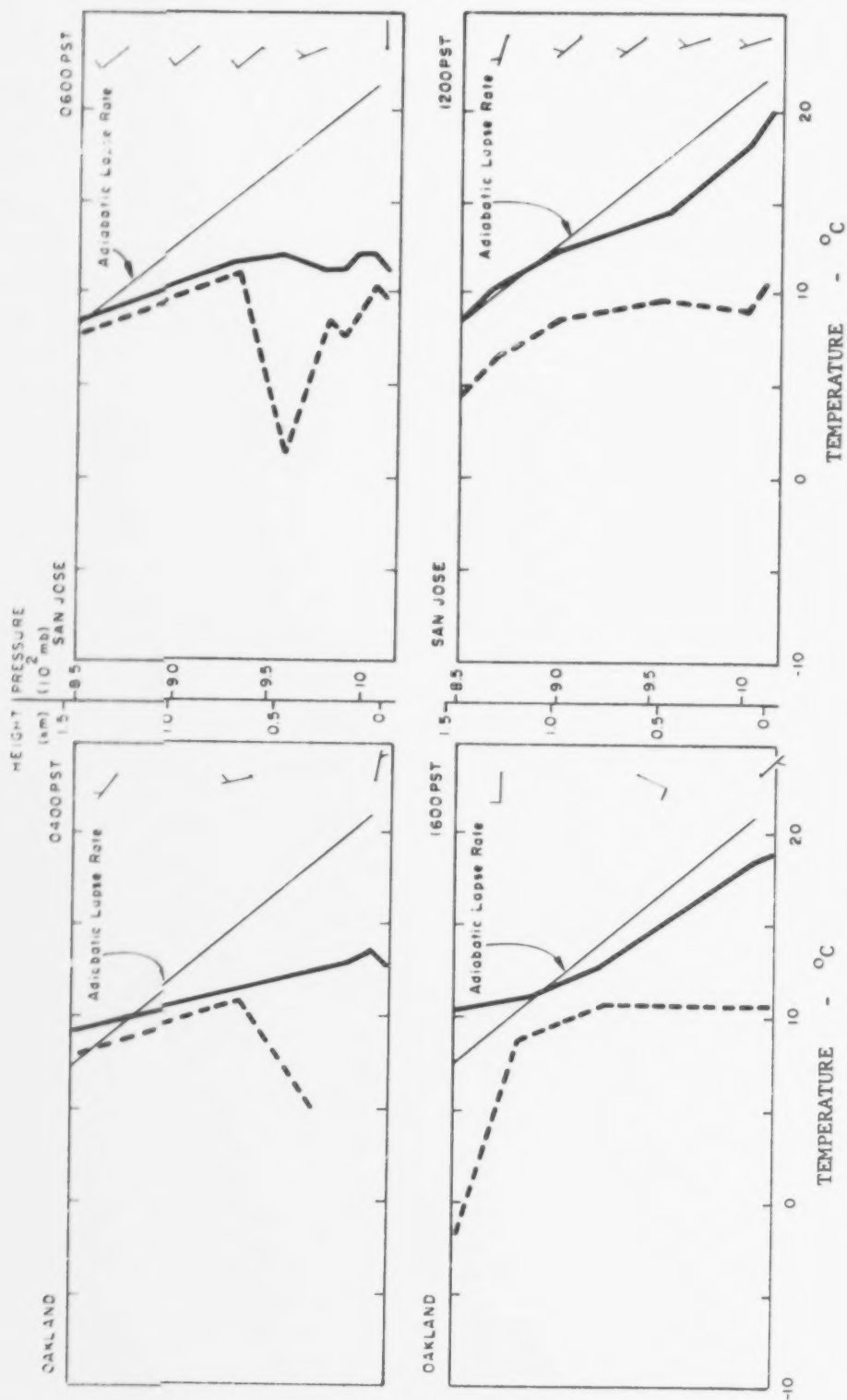


FIGURE 17 RAWINSONDE TEMPERATURE AND DEW POINT OBSERVATIONS, 2 NOVEMBER 1972  
(Temperature —, Dew Point ---)

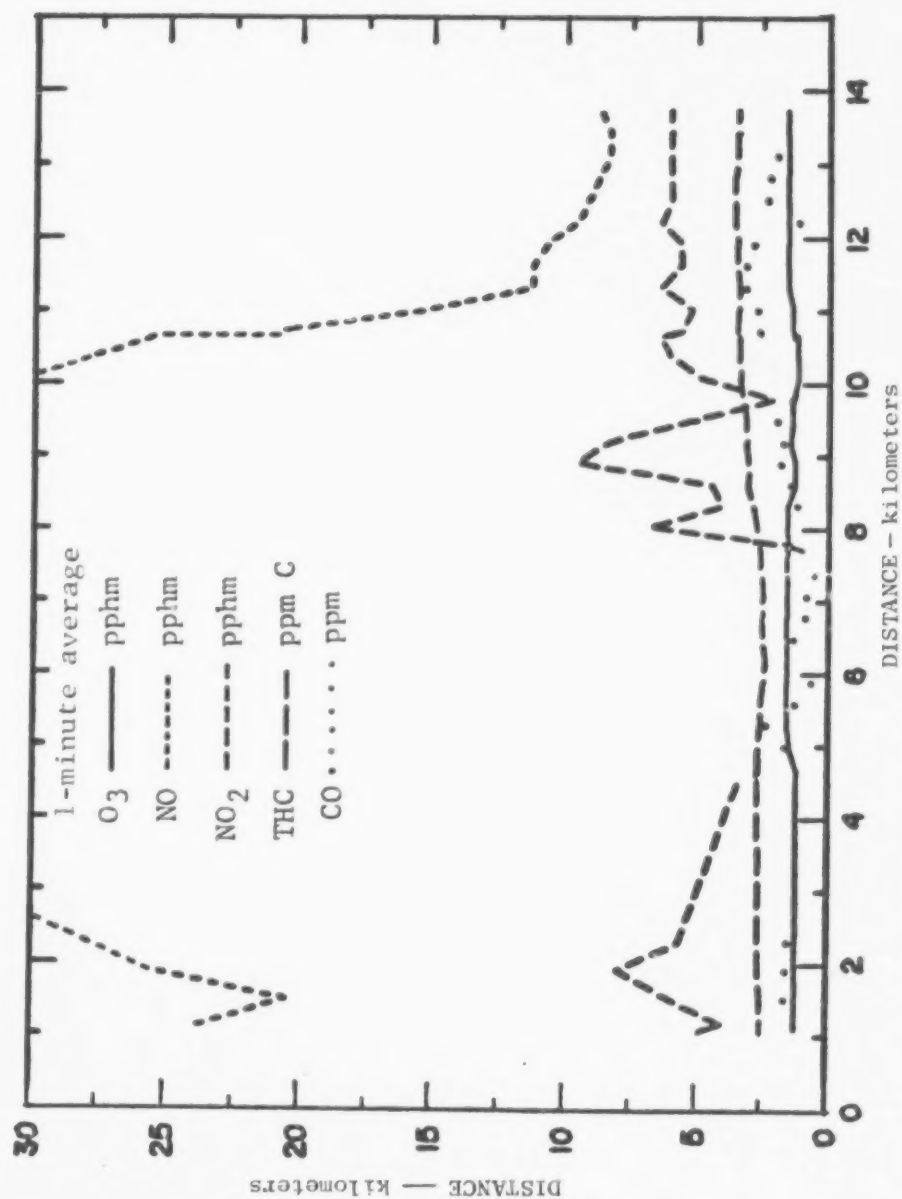


FIGURE 18 POLLUTANT CONCENTRATIONS OBSERVED DURING TRAVERSE OF THE BAY, WEST TO EAST, 2 NOVEMBER 1972, 0843 to 0957 PST

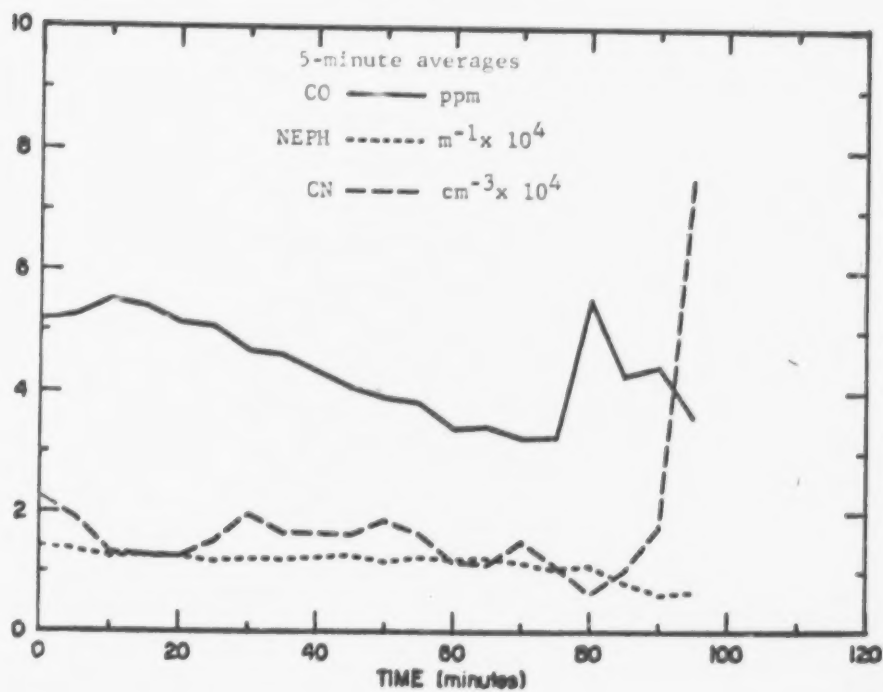
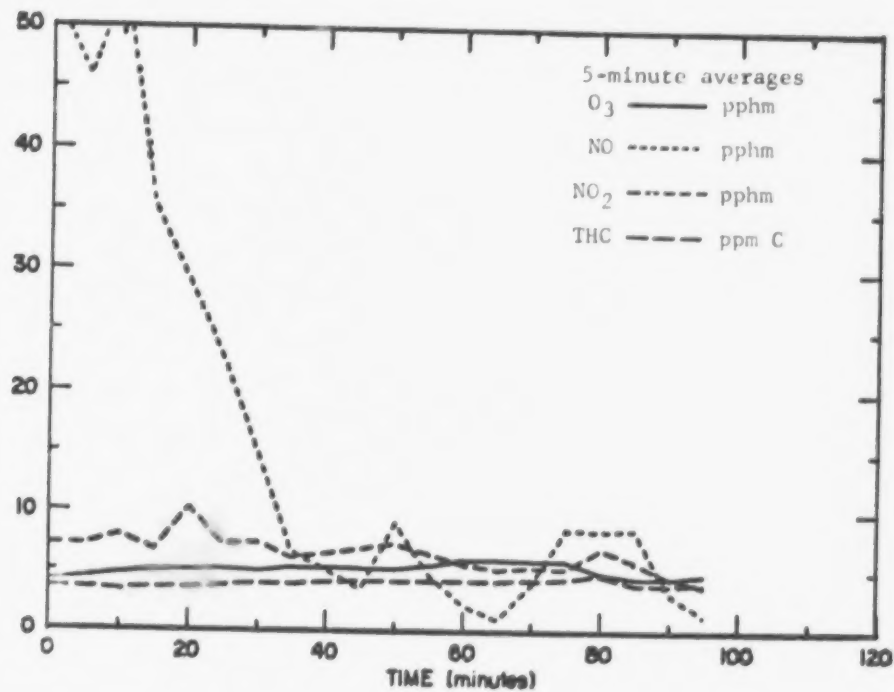


FIGURE 19 POLLUTANT CONCENTRATIONS OBSERVED DURING TETROON RUN,  
2 NOVEMBER 1972, 1141 to 1316 PST

By noon, these inversions were completely dissipated by surface heating and mixing. The dry adiabatic lapse rate prevails into the evening Oakland sounding.

A slow traverse was made from Oyster Point to San Leandro Harbor. The houseboat was stopped frequently during the traverse for 5-minute intervals. A 5-minute average of measured pollutant concentrations was obtained during these intervals. Small helium-filled balloons were released to determine wind direction, and wind speeds were measured with an anemometer. The houseboat headed directly into the wind at all times. The NO concentration in the center of the Bay reached 60 pphm; concentrations were observed near the shoreline. The concentration of NO<sub>2</sub>, O<sub>3</sub>, THC, CO, and CN did not increase proportionately in the center of the Bay. The NO to NO<sub>2</sub> ratio was greater than 10, which is characteristic of freshly polluted air. The source of this NO is probably not houseboat exhaust, since increases in CO, CN, and THC concentrations did not occur simultaneously.

The simple Gaussian plume model described previously was used to estimate the contribution of NO from the PG&E power plant plumes. The maximum NO concentration near the houseboat was predicted to be 5 pphm, which is too low to satisfactorily explain the observed concentrations. The meteorological data implied a general northwesterly air flow on the upper half of the Bay. Therefore, the source of the pollution is probably San Francisco and not San Jose.

A tetroon released at 1123 near the center of the Bay rose to about 150 meters altitude, but remained in the vicinity of the release point for about 40 minutes due to stagnation. To avoid contamination from the houseboat exhaust, the houseboat was navigated in circles and figure eights under the tetroon. A tethered helium-filled balloon was

used to determine the resultant wind direction so that a relative forward wind speed could be maintained at all times. The high NO concentrations observed between 1141 and 1211 are ascribed to the houseboat. Spikes in the CN concentrations were observed when the houseboat crossed its own exhaust plume. Similar spikes in NO concentration were not observed simultaneously because the time constant of the NO<sub>x</sub> analyzer is considerably longer than that of the CN counter.

At about 1200, a stronger marine air flow carried the tetroom south over the San Mateo Bridge (1200 to 1316). The houseboat passed under the San Mateo Bridge at 1302. Between 1200 and 1302 the O<sub>3</sub> increased, indicating photochemistry was occurring. As the houseboat passed under the San Mateo Bridge, the expected increases in NO, CO, THC, and CN as well as a decrease in O<sub>3</sub> were observed. Figure 20 is a plot of 1-minute average pollutant concentrations plotted against distances from the San Mateo Bridge. There was an increase of THC, CO, NO, and NO<sub>2</sub> as the houseboat passed under the bridge. The THC, CO, and NO are from automobile emissions. A significant portion of the NO<sub>2</sub> is from the reaction of NO and O<sub>3</sub>. There is a corresponding decrease in O<sub>3</sub> concentration. It is not clear why O<sub>3</sub> decreases 2 pphm while NO<sub>2</sub> increases 6 to 9 pphm, unless a portion of the NO emissions on the bridge are rapidly oxidized by O<sub>2</sub> to NO<sub>2</sub>. Finally, the peak in the NO concentration observed before the bridge cannot be easily explained because CO, THC, and CN did not increase simultaneously, thereby ruling out both bridge and houseboat exhaust.

The chemical analysis of glass fiber filters collected on 2 November is summarized in Table 6. The chemical composition of the particulate is characteristic of aged aerosols. The observation of 5 to 10 percent sulfur was unexpected since there are few SO<sub>2</sub> emissions in the Bay Area; presumably, it comes from sea spray. The chloride to sulfur ratios are low, further supporting the conclusion that the

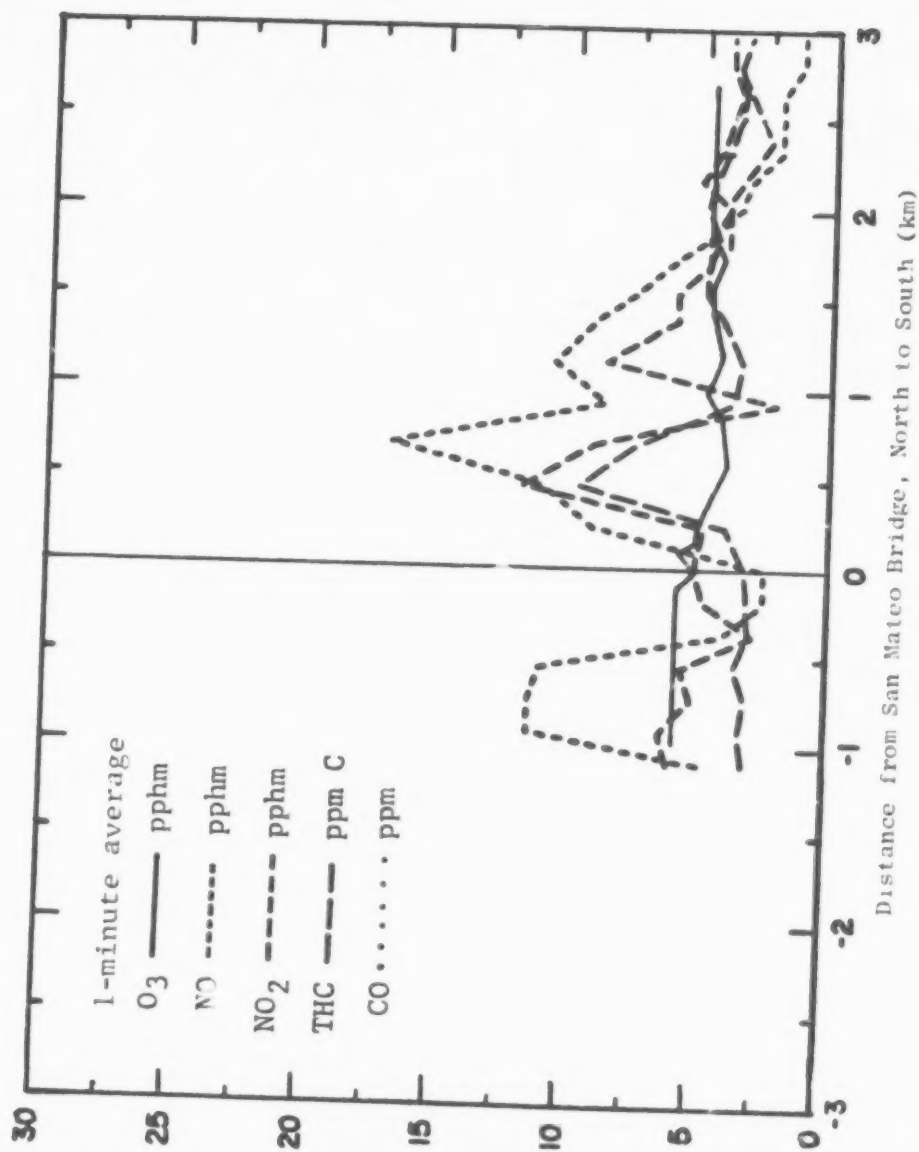


FIGURE 20 POLLUTANT CONCENTRATIONS OBSERVED IN VICINITY OF SAN MATEO BRIDGE DURING TETROON RUN, 2 NOVEMBER 1972, 1253 TO 1327 PST

Table 6

CHEMICAL ANALYSES OF PARTICULATE MATTER  
COLLECTED ON GLASS FIBER FILTERS,  
2 NOVEMBER 1972

| Time (PST)   | Mass Loading<br>( $\mu\text{g}/\text{m}^3$ ) | Chemical Composition ( $\mu\text{g}/\text{m}^3$ ) |        |          |      |
|--------------|----------------------------------------------|---------------------------------------------------|--------|----------|------|
|              |                                              | Nitrate                                           | Sulfur | Chloride | Lead |
| 0833 to 1120 | 108                                          | 10.8                                              | 6.0    | 1.0      | 2.4  |
| 1123 to 1317 |                                              |                                                   |        |          |      |
| 1633 to 1745 | 194                                          | 24.7                                              | 17.3   | 3.1      | 2.6  |

aerosols were predominately of anthropogenic origin and not sea salt. From 1633 to 1745, aerosol was collected near San Francisco during a tetroon run from San Francisco to the Alameda Naval Air Station. The increase in mass loading is probably due to the lack of dilutional effects observed on other days when the particulate samples were collected farther from the sources.

Lundgren impactor samples collected on 2 November 1972 were analyzed and reported by AIHL. The results of their analyses are included in Appendix F. In this report, the chemical composition and size distributions of the 2 November aerosol was compared to aerosol data analyzed and reported on previous studies in the Bay Area. The general conclusion based primarily on the bromine to lead ratios, was that the aerosols are well aged. The collected particulate was not analyzed to determine the organic constituents. Since little or no secondary aerosol formation was observed during this research program, photochemical changes in aerosol composition cannot be determined.

The electronic scattering cross-section analysis spectra for sulfur indicated that the sulfur-containing particulate trapped on the after filter (particles less than about 1 micron) was 70 percent sulfate. The sulfur present in the larger particles was almost 100 percent in

the form of sulfate. We can only speculate about the sources of non-sulfate sulfur. These sources could be anthropogenic or biological, for example, the decomposition of organic materials on the floor of the Bay. More definitive data are clearly required to identify the sources of nonsulfate sulfur particulate material.

The particulate collection data obtained in the research program demonstrate the feasibility of collecting satisfactory samples from a houseboat. However, SRI believes that the following changes in experimental technique are warranted for future programs:

- More frequent hi-vol filters should be collected.
- Total filters should be collected on Gelman GA-1 filters for comparison to the Lundgren data.
- A one-stage Lundgren type of impactor plus an after filter would probably give adequate data at a considerable reduction in analytical costs.
- The samples should be collected over as short a time as possible to improve the resolution of the data.

## VI PRELIMINARY ANALYTICAL RESULTS BASED ON COMBINED DATA FROM SELECTED SAMPLING DAYS

### A. Usefulness of the Data

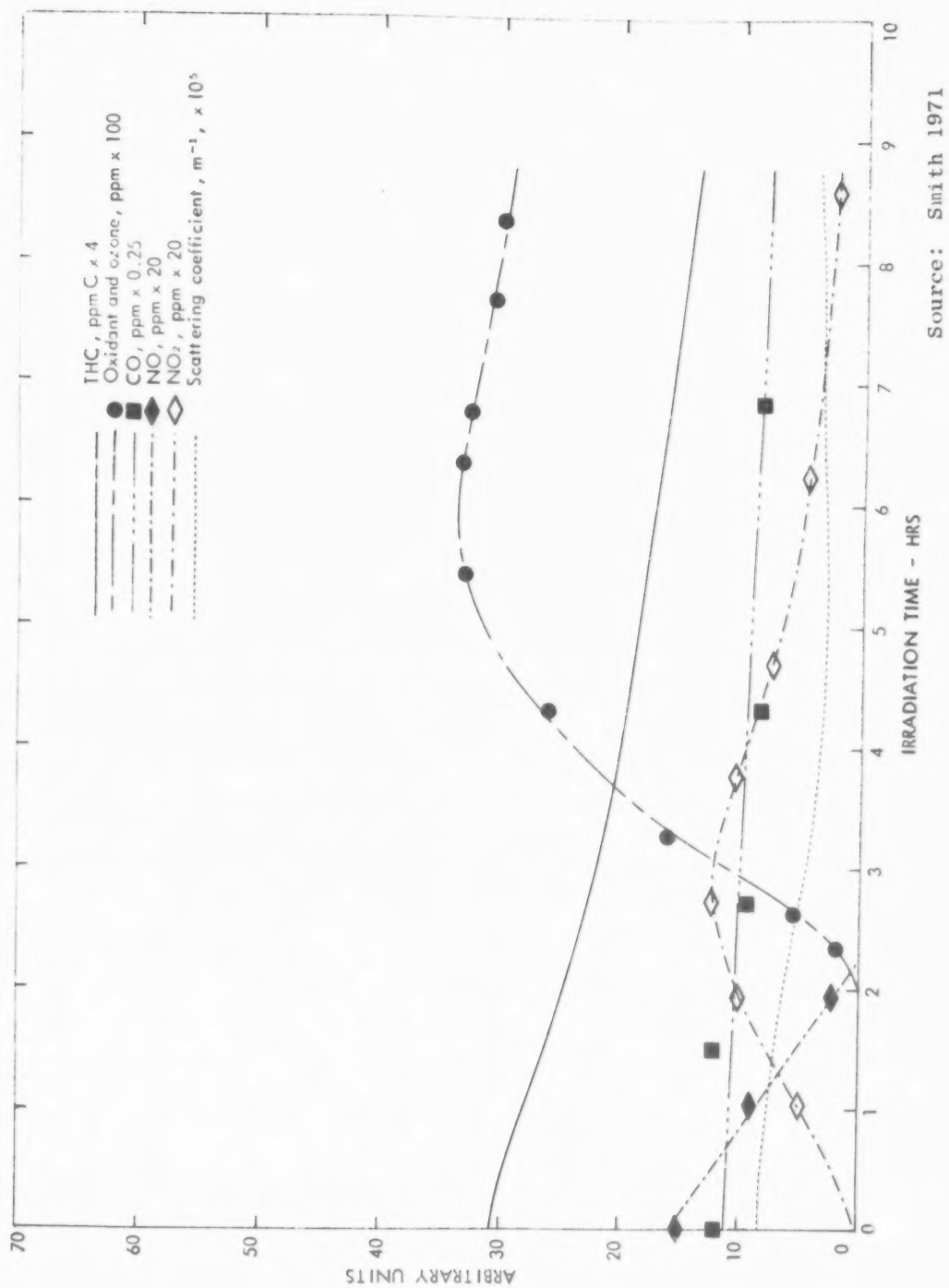
A primary objective of this research program was to collect data that will help provide a basis for defining atmospheric photochemical processes and will provide the background data required to evaluate a simulation model of photochemical smog.\*

To critically assess the degree to which the first of these objectives was accomplished, the analogy of the San Francisco Bay and a large smog chamber was considered. The conclusion is a qualified agreement as to the validity of the analogy. The data must be critically examined to see if photochemical changes occur and, if so, how similar they are to smog chamber experiments. This is admittedly a difficult task because, due to the meteorological conditions of the autumn of 1972, it was not possible to make long tetraon runs and there was little smog.

First, let us consider the changes in pollutant concentrations that occur during a typical chamber experiment. For an example, the data in Figure 21 were obtained during an earlier SRI project.<sup>13</sup> A mixture of 7.5-ppm C automobile exhaust, generated by using a 93-octane gasoline of 55 percent paraffins, 11 percent olefins and 33 percent aromatics, and 0.75 ppm NO was irradiated in the SRI smog chamber. While the concentrations are higher than observed on the Bay, several general characteristics of a static smog chamber reaction are depicted in this example. The first noticeable chemical change is that:

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\*L. A. Cavanagh, R. C. Robbins, J. H. Smith, SRI Proposal ERU 72-71, "Atmospheric Photochemical Smog Measurements Over San Francisco Bay"



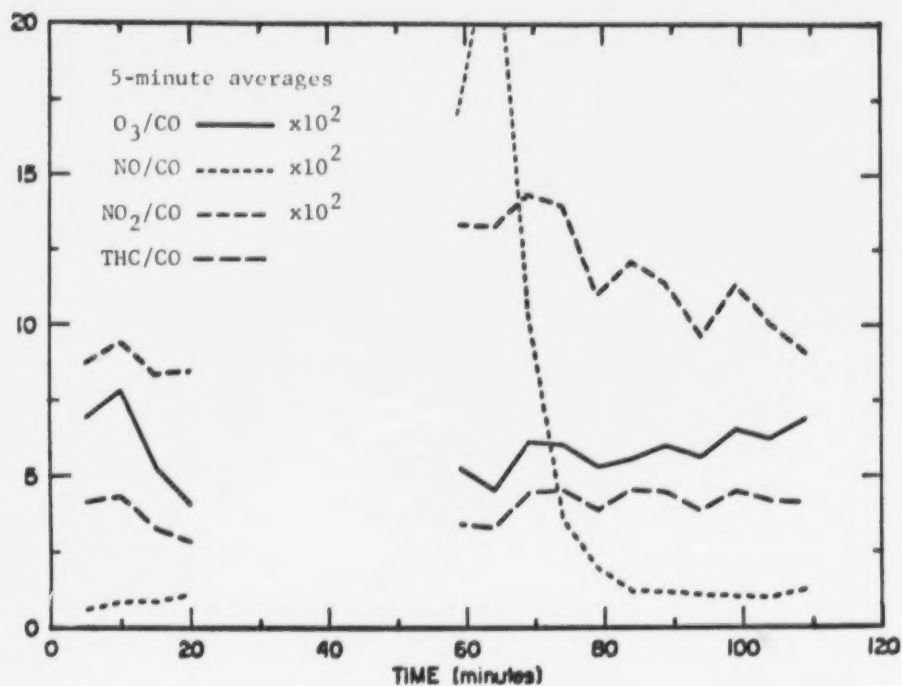
Source: Smith 1971

FIGURE 21 REPRESENTATIVE SMOG CHAMBER RUN IN SRI CHAMBER, AUTOMOBILE EXHAUST  
(7.5 ppm C) and NO (75 pphm)<sup>10</sup>

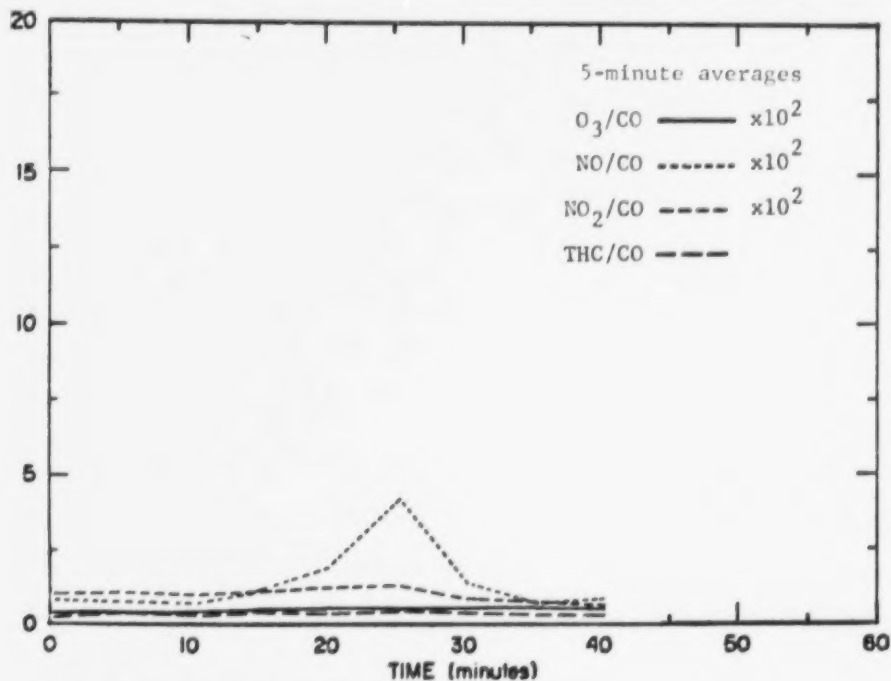
- NO falls to nearly zero
- NO<sub>2</sub> increases proportionately, reaches a maximum value less than or equal to the initial NO concentration, then decreases slowly,
- Oxidant, which is primarily O<sub>3</sub>, builds up only after the NO<sub>2</sub> maximum. A maximum O<sub>3</sub> concentration, followed by a slow decrease, is observed.
- The THC concentrations decrease throughout the run to approximately one half of the initial concentrations. GC analysis showed that only reactive hydrocarbons, such as olefins and substituted aromatics, react within the experimental time frame.
- The apparent decrease in CO is due to dilution of the chamber air as the result of replacement of the air removed by the air quality instrumentation.
- Although this example does not clearly show it, formation of secondary aerosols usually parallels O<sub>3</sub> formation.

Since auto emissions of nitrogen oxide are almost exclusively NO, the value of the NO to NO<sub>2</sub> ratio gives a crude but quick estimation of the age of air mass. High NO to NO<sub>2</sub> ratios, greater than 1.0, are representative of fresh air masses; low NO to NO<sub>2</sub> ratios, less than 1, are found in well-aged air masses. Generally, higher O<sub>3</sub> concentrations are associated with lower NO to NO<sub>2</sub> ratios.

In the atmosphere, dilutional effects can mask photochemical changes. Since CO is essentially inert at these concentrations, we can correct for the dilutional effects by dividing the other pollutant concentration by the CO concentration. Figure 22 is a plot of the ratios of NO, NO<sub>2</sub>, O<sub>3</sub>, and THC to CO for the 5-minute averages during the selected sampling days.

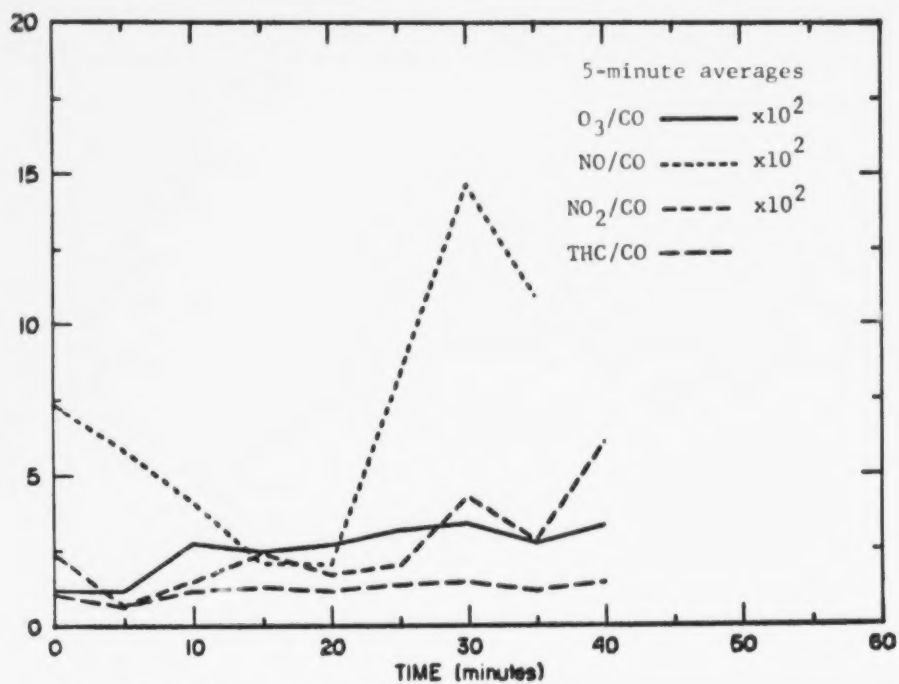


(a) 21 September 1972, 1037 to 1226 PST

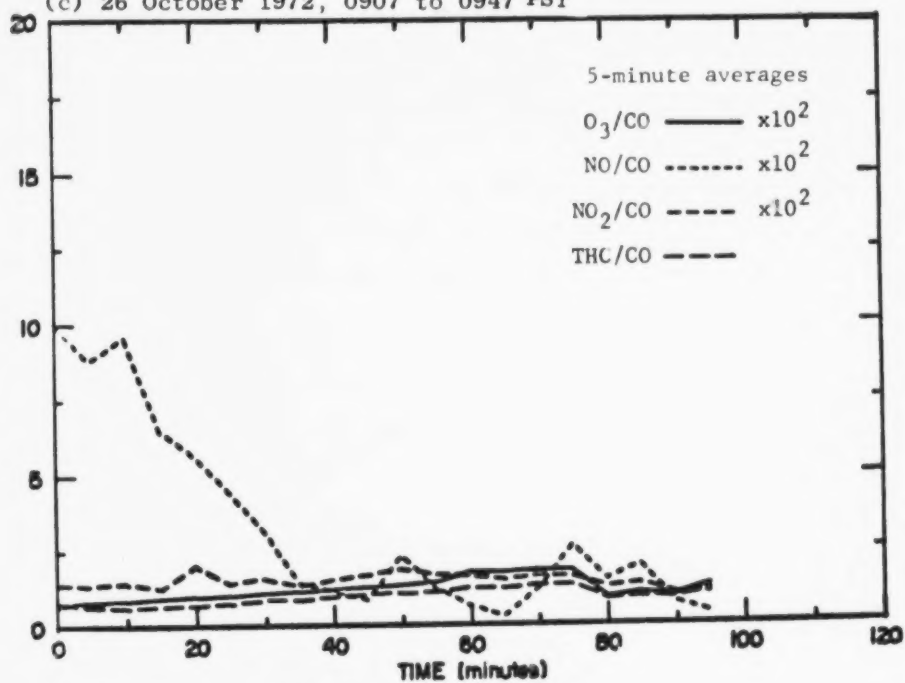


(b) 25 October 1972, 1138 to 1218 PST

FIGURE 22 RATIOS OF POLLUTANTS TO CO CONCENTRATIONS OBSERVED DURING TETROON RUNS (5-minute averages)



(c) 26 October 1972, 0907 to 0947 PST



(d) 2 November 1972, 1141 to 1318 PST

FIGURE 22 RATIOS OF POLLUTANTS TO CO CONCENTRATIONS OBSERVED DURING TETROON RUNS (5-minute averages) (Concluded)

On 21 September, the smog observed from 1034 to 1057 when the houseboat was near San Francisco, is clearly well aged. Significant  $O_3$  concentrations are present and the NO to  $NO_2$  ratio is low ( $\sim 0.2$ ). At this time, freshly polluted air including CO was injected into the air mass (see Figure 4). At 1036, the houseboat passed through a portion of the PG&E stack plume from Potrero Point. Since there is comparatively little CO in the plume, the ratio plot remains valid.

The pollutant ratio plot, Figure 22a, clearly shows the occurrence of classical photochemical smog activity. The  $NO_2$  may be at a maximum from 1036 to 1141 since it decreases steadily after this time. The  $O_3$  also increases, while the THC and NO are nearly constant. The photochemical events occurring on 21 September from 1036 to 1220 correspond to similar events occurring after 3 to 4 hours of irradiation in the smog chamber experiment shown in Figure 21. If the tetroon had not descended at 1220, the  $O_3$  maximum might have been observed.

Judging from the NO to  $NO_2$  ratio, the air masses followed on 21 September, 25 October, and 2 November  $[NO]/[NO_2] \sim 1$  were well aged, while that for 26 October  $[NO]/[NO_2] \sim 3$  was very fresh. Less dramatic photochemical activity was observed during the last three selected tetroon runs. Even though the NO to CO ratio sometimes rose sharply during these runs, the ratios of  $NO_2$  to CO and  $O_3$  to CO apparently were not affected. Since the CO and CN concentrations did

---

Fresh pollutants from the city were injected into the tetroon-marked air mass containing aged pollutants as it passed over the eastern shore line. The  $O_3$  in the well-aged air mass oxidizes the NO added by the city to  $NO_2$ . The higher initial  $NO_2$  concentration causes the  $NO_2$  maximum to be observed sooner than would be the case if the NO were added to clean air. Unpublished data previously obtained with the SRI smog chamber have shown that under similar conditions a second  $NO_2$  maximum is rapidly reached after addition of NO to a well-aged irradiated mixture of mesitylene and NO.

not rise at the same time, exhaust contamination was ruled out. However,  $O_3$  concentrations do not decrease and  $NO_2$  concentrations do not increase in the presence of high NO concentrations that would be expected from the reaction  $NO + O_3 \rightarrow NO_2 + O_2$ . There is no obvious explanation for these observations.

The rates of formation or loss of  $NO_2$ ,  $O_3$ , and THC were calculated and corrected for dilutional effects by multiplying the calculated rates by the ratio of the initial to the final CO concentrations (Table 7). The calculated formation rates of  $NO_2$  and  $O_3$  are approximately the same as the rates calculated from the smog chamber data in Figure 21. However, the THC rate of disappearance is an order of magnitude slower in the atmosphere than was observed in the SRI smog chamber.

Table 7  
POLLUTANT FORMATION OR LOSS RATES  
(pphm/min)

| Date         | $NO_2$ | $O_3$ | THC   |
|--------------|--------|-------|-------|
| 21 September | 0.17   | 0.05  | 0.02  |
| 25 October   | 0.0    | 0.01  | -0.01 |
| 26 October   | 0.18   | 0.11  | 0.03  |
| 2 November   | -0.07  | 0.02  | 0.0   |

In two cases, the THC concentration increases very slowly, contrary to smog chamber observations. The increase may be an artifact of the simple approximation procedure.

A valid comparison of the Bay Area to a large smog chamber can only be made on days when the meteorological conditions are conducive to smog formation. These conditions occur only with a northwesterly air flow down the axis of the Bay at velocities of less than 5 to 8 mph. These same conditions are also the only ones that would permit tetraon flights of 4 to 6 hours. These long reaction

times would permit the development of significant photochemical activity. The only days when these conditions were observed during the fall of 1972 were 21 September and 2 November. The data for these days show definite photochemical activity even though the ambient temperatures were below 70<sup>0</sup> F. Under conditions of extreme stagnation, longer runs would be possible, but the likelihood of houseboat exhaust contamination would also increase significantly.

Formation of secondary (photochemical) particulate matter was not observed during the selected tetron runs, based on the nephelometer readings. However, this study conclusively demonstrated that reliable particle size distribution, mass loading, Lundgren impactor, and high volume sampler data can be collected on a houseboat mobile laboratory.

In view of the lack of significant photochemical activity, these data are of limited usefulness for model validation. The data for 21 September showed the greatest photochemical activity. The failure of the tetron prevented us from collecting 1 to 2 hours of additional data. A longer tetron run would have greatly increased the usefulness of this day's data.

The data collected on 2 November should be useful in two ways. First, data were collected that demonstrated photochemical activity at concentrations approximating the clean air standards established by the Environmental Protection Agency. Second, the data collected between 1253 and 1327 PST (Figure 2C) are a unique example of the effect of pollutants from a line source of automobile traffic injected into an air parcel containing well-aged pollutants at near background concentrations.

The remainder of the data were obtained under conditions not conducive to long tetron runs. In shorter tetron runs, significant changes in pollutant concentrations and secondary aerosol composition due to chemical reactions cannot be observed. Therefore, such data will be less useful for model verification.

## B. Mass Balance

In its simplest terms, a mass balance in a photochemical smog reaction will be achieved if the mass of carbon and nitrogen (from HC and  $\text{NO}_x$ , respectively) consumed during the reactions equals the change in the mass of carbon and nitrogen in the products, which are primarily aerosols. To determine the carbon mass balance, the carbon content of the gaseous pollutants and the collected aerosol must be determined. The carbon content of the gaseous pollutants was determined through measurement of total hydrocarbon and through hydrocarbon distribution measurements by gas chromatography. Although the on-board gas chromatograph (see Section "Hydrocarbon Distribution" beginning page B-19, in Appendix B) did not provide adequate resolution of the ambient organics, the laboratory analysis of cryogenically collected samples by gas chromatography provided excellent data. The collected aerosol was analyzed for total C but the organic and inorganic contribution cannot be distinguished. The analysis for carbon is not available from the sticky foil stage of the Lundgren impactor (1B) or from the after filter due to interference from the substrate. The measurement of distribution of organics within the collected aerosol was proposed but not funded by the ARB.

The nitrogen balance requirements were better satisfied by the experimental design of the program than that of carbon balance. However, to obtain a true nitrogen balance, ammonia must be measured in the gaseous phase and ammonium content of the collected particulates must be determined. The measurement of gaseous ammonia or the ammonium content of aerosol is not required as input to photochemical simulation models.

Under conditions where a reasonable amount of photochemical activity is taking place, a carbon mass balance can be approached without differentiating inorganic and organic carbon content of collected particulate. Under the same conditions, a nitrogen mass balance can be approached through measurement of nitrogen oxides and the nitrate content of par-

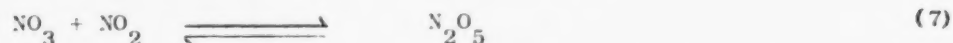
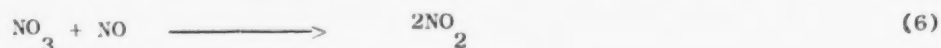
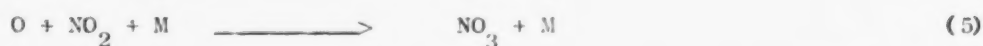
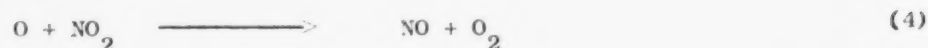
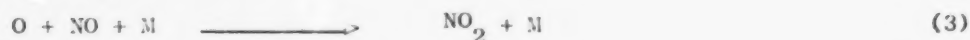
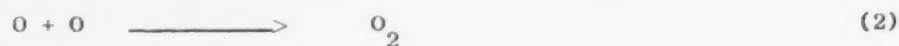
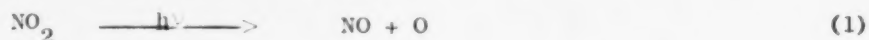
ticulate. However, in the absence of sufficient photochemical activity to produce secondary aerosols and conditions when wind direction and velocity do not permit long tracking times of the tetroon, a meaningful mass balance cannot be obtained. In the Bay Area, intense photochemical activity only occurs under meteorological conditions conducive to long-term tracking of the tetroon.

On 21 September, the sample day that the maximum photochemical activity was observed, no aerosol formation was observed (Figure 5) even when corrections for dilutional effects were applied. However, the concentration of  $\text{NO}_2$  decreased more rapidly than could be attributed to dilutional processes. This implies that secondary aerosol was formed. As previously discussed, the observed aerosol decrease also is greater than can be attributed to dilutional processes. Thus, the consumption of  $\text{NO}_2$ , though implying aerosol formation, cannot be verified by a corresponding formation of aerosol. The aerosol loss mechanisms apparently dominate aerosol formation by HC and  $\text{NO}_x$ . It is possible that with more accurate temperature and relative humidity measurements, combined with complex calculations of water loss from the particles and of aerosol coagulation, a mass balance could be achieved at an intensity of photochemical smog activity comparable to that observed on 21 September 1972. However, measurements made during intervals of significantly more intense photochemical activity would be required to realistically verify that a mass balance is achieved.

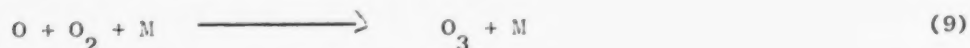
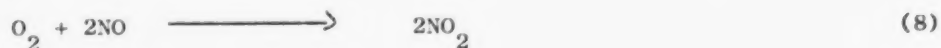
The photochemical activity observed during the other sampling days was significantly less than that of 21 September, and hence the measurement data are not applicable to mass balance determinations.

### C. The $\frac{[\text{NO}][\text{O}_3]}{[\text{NO}_2]}$ Ratio

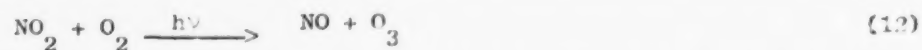
The important chemical reactions of nitrogen oxides and reaction products in the absence of  $\text{O}_2$  are:



In the presence of  $\text{O}_2$ , these reactions are also important:



The rate constants are such that, in air, reactions (1), (9), and (11) are much faster than any of the others listed above and also faster than the reactions of  $\text{O}_3$  and  $\text{O}$  with HC. The rate of reaction (9) is collision controlled because of the high concentration of  $\text{O}_2$  in the air. Reactions (1) and (7) can be combined to give reaction (12)



The rate of reaction (12) is controlled by the photodissociation rate of  $\text{NO}_2$ , which in turn depends on the wavelength and intensity of

the incident light. The photodissociation rate of reaction (1) will be the product of the solar intensity  $k_a$  and the quantum yield  $\Phi$ , which are both a function of wavelength. Integration over the solar spectrum gives

$$k_1 = \int_{\lambda} k_a(\lambda) \times \Phi(\lambda) d\lambda$$

the photodissociation rate  $k_1$ .

Reactions (11) and (12) can be combined and written as equilibrium (13).



An equilibrium constant  $K$  for reaction (13) can be defined by

$$K = \frac{k_1}{k_{11}} = k_a C = \frac{[\text{NO}][\text{O}_3]^*}{[\text{NO}_2]} \quad (14)$$

Since the spectral distribution of sunlight is nearly a constant,\*\* it has been suggested by Leighton<sup>13</sup> that the value of  $K$  should be directly related to  $k_a$ . The proportionality factor  $C$  will be a constant provided the spectral distribution of the sunlight and the temperature are constant. Therefore, it should be possible to calculate the value of  $k_a$  from the measurement of the concentration of  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{O}_3$ .

In the presence of hydrocarbons, the rate of  $\text{NO}$  oxidation and  $\text{O}_3$  formation increases. The  $\text{O}_3$  and  $\text{NO}_2$  concentrations are both higher than would be calculated from equilibrium reaction 13. Therefore, there is no a priori reason to predict that the value of Equation 14 should be equal to the value calculated in the absence of hydrocarbons.

\*The square brackets indicate the concentration of the species inside the brackets.

\*\*The amount of particulate matter in the air will have a slight effect on the indirect portion of sunlight, because blue light is scattered more than red light. This effect is small in the Bay Area, due to the low concentrations of particulate observed.

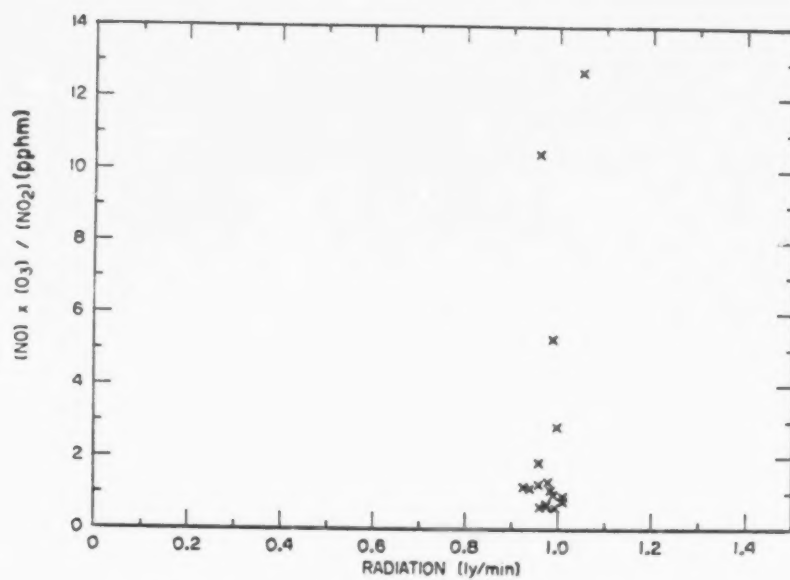
The first analysis of the solar intensity measurements resulted in data where the total solar intensity exceeded that expected for the sampling days.\* Furthermore, the calibration of the instrument using an Eppley pyranometer showed that the output of the instrument was zero at 0.67 Langleys/minute or lower because the sensing element was recessed in the housing. A reexamination of the data showed that the digital voltmeter of the Nova computer system over ranged above 1.0 volt (that is, a 1.5 volt input would be read as 0.5 volt). A computer program was written to correct for these errors. The resulting data for the four selected days are presented in Figure 23. The data for the four days were also combined and are presented in Figure 24.

A preliminary analysis of the houseboat data has been made using the four selected days as examples. The  $O_3$  concentrations were recorded every 30 seconds. Each recorded value is an average; the measured values were updated every minute. Solar intensity was recorded every 30 seconds, but these values must be smoothed by averaging to correct for the roll of the boat. For this preliminary analysis we have used the 5-minute averages of  $NO$ ,  $NO_2$ , and  $O_3$  to calculate  $K$  and have compared these values to the 5-minute average solar intensity measured on the four selected days. A linear least-squares fit was applied to the data. The correlation coefficients of the ratio with solar intensity (Table 8) are low. This result agrees with the conclusions reached earlier in this section.

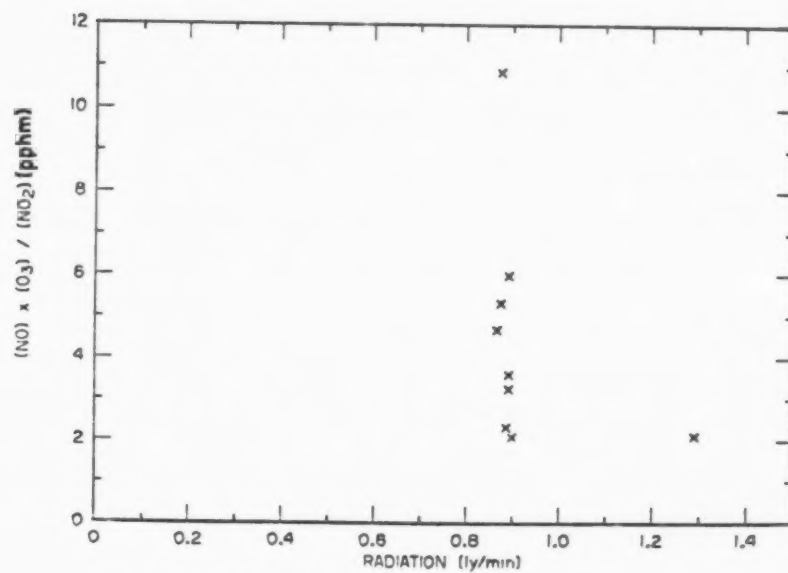
Plots of  $K$  versus time for each day suggested that  $K$  may correlate well with  $NO$  concentration. Plots of  $K$  versus  $NO$  concentrations were made (Figure 25), and the data for each of the four selected days were combined (Figure 26).

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\*The expected maximum solar intensities are: 21 September, 1.4 Langleys/minute; 25 October, 1.25 Langleys/minute; 26 October, 1.15 Langleys/minute; 2 November, 0.95 Langleys/minute.

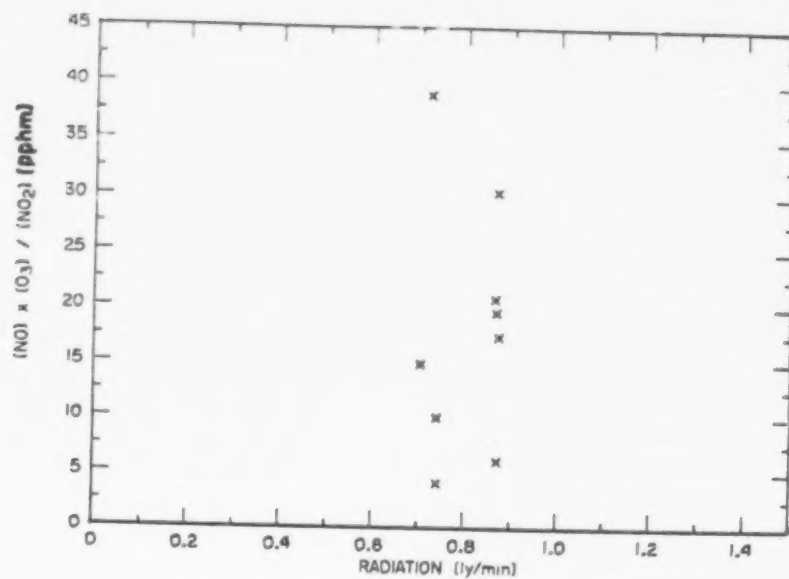


(a) 21 September 1972, 1037 to 1226 PST

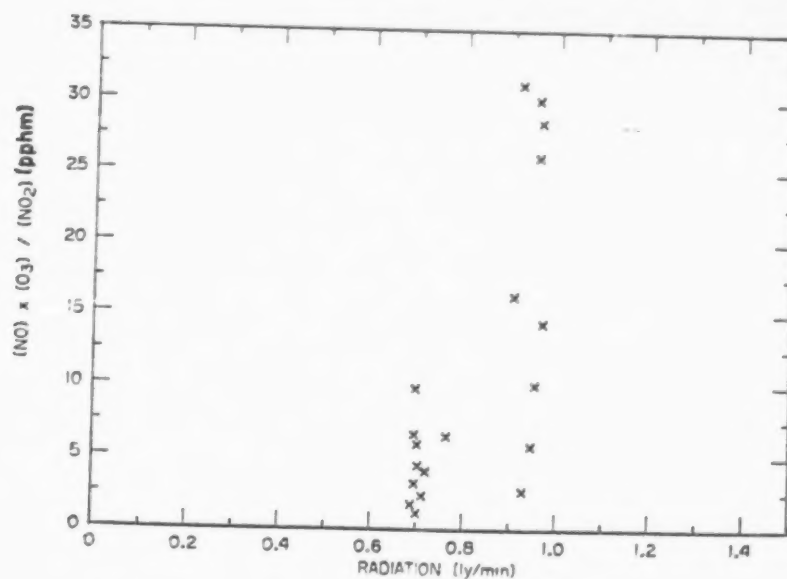


(b) 25 October 1972, 1138 to 1218 PST

FIGURE 23  $[NO] [O_3] / [NO_2]$  RATIOS VERSUS SOLAR INTENSITY FOR TETROON RUNS (5-minute averages)



(c) 26 October 1972, 0907 to 0947 PST



(d) 2 November 1972, 1141 to 1316 PST

FIGURE 23  $\frac{[NO][O_3]}{[NO_2]}$  RATIOS VERSUS SOLAR INTENSITY FOR TETROON RUNS (5-minute averages) (Concluded)

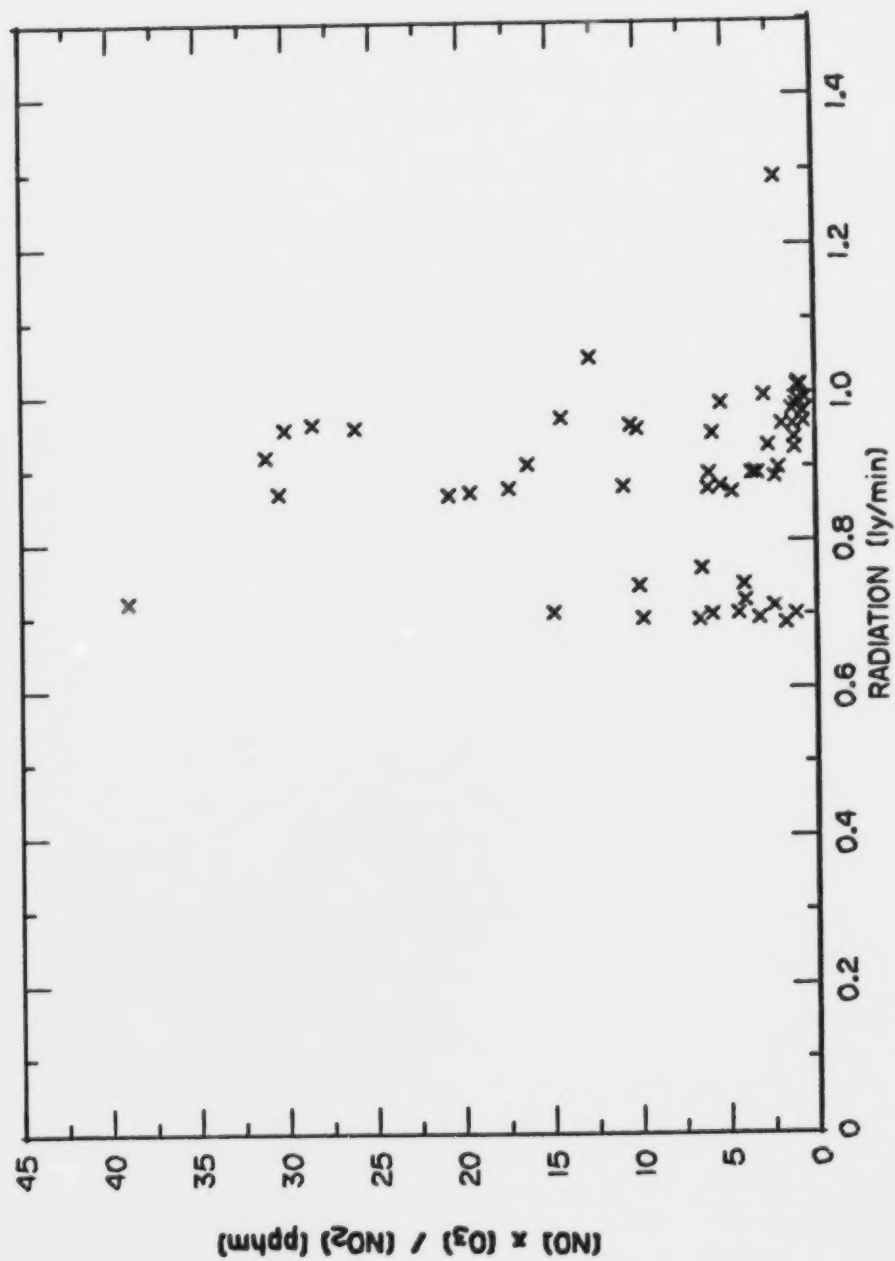
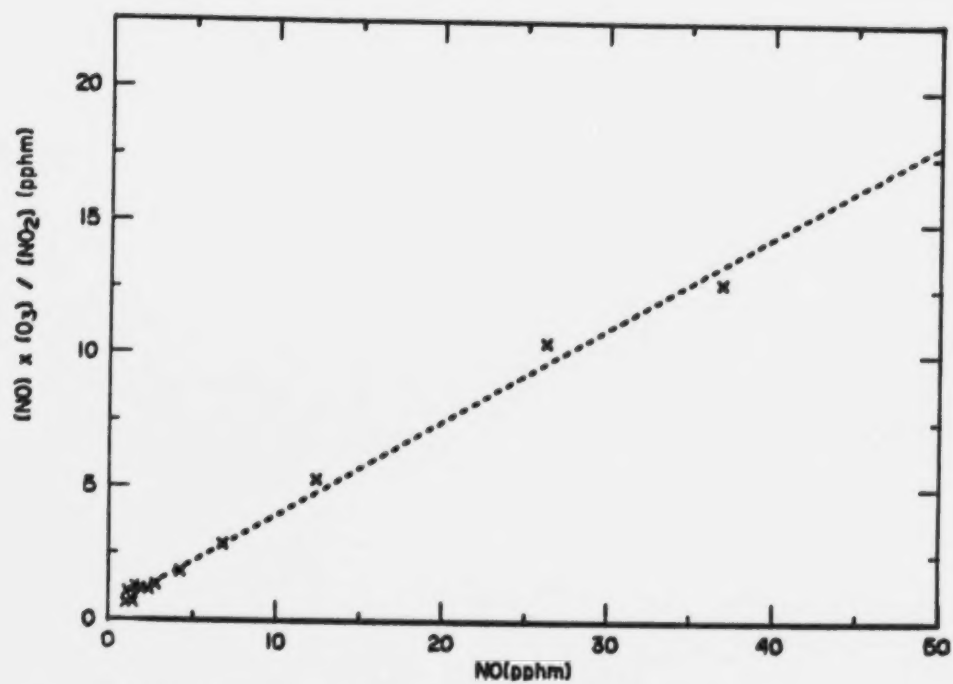
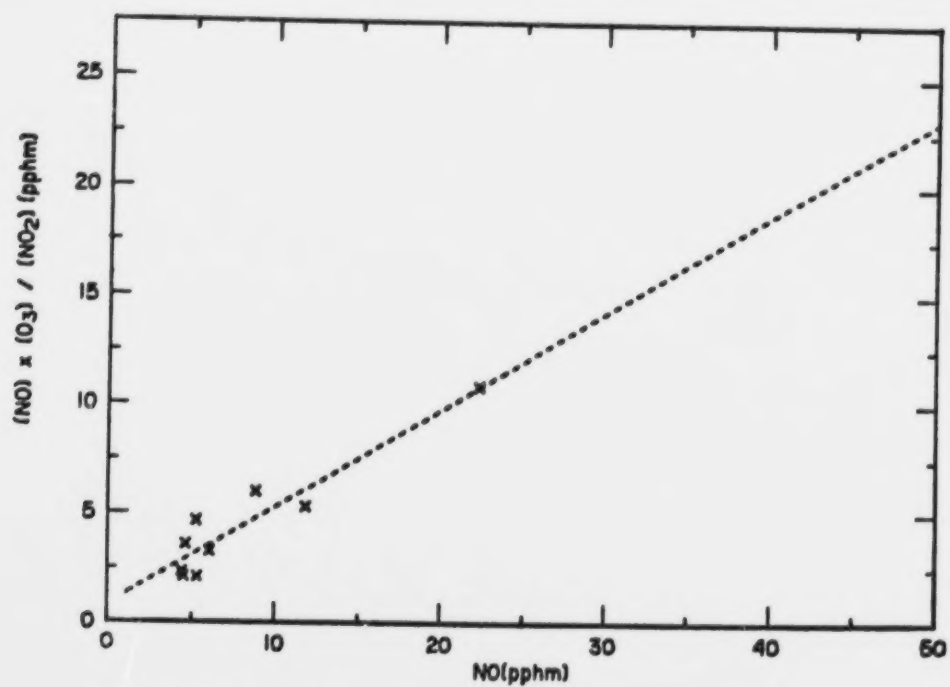


FIGURE 24  $[NO] [O_3] / [NO_2]$  RATIOS VERSUS SOLAR INTENSITY, COMBINED DATA FROM FIGURE 23

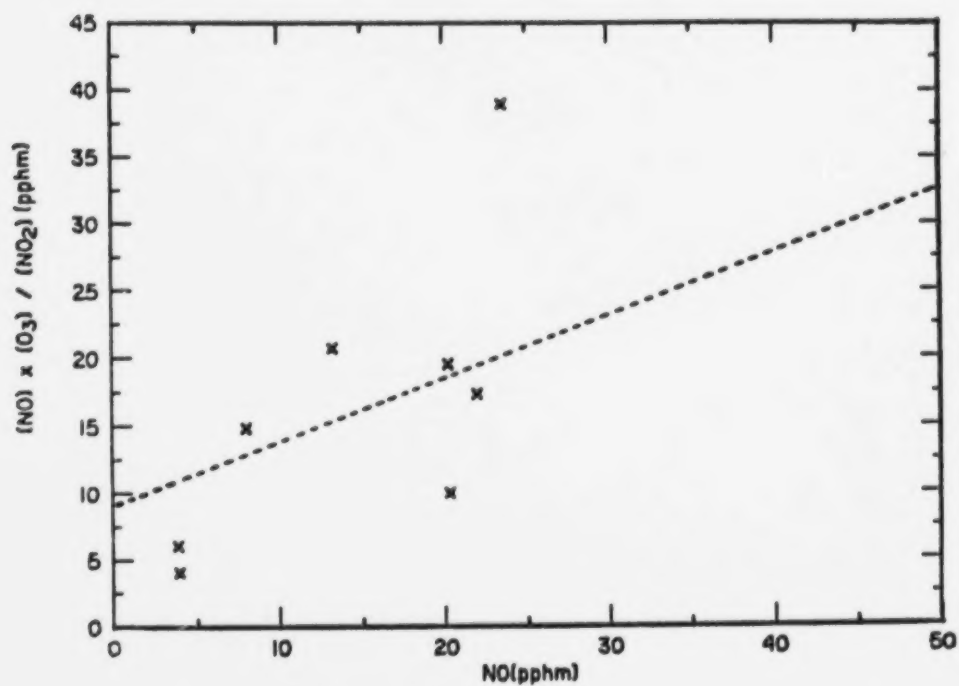


(a) 21 September 1972, 1037 to 1226 PST

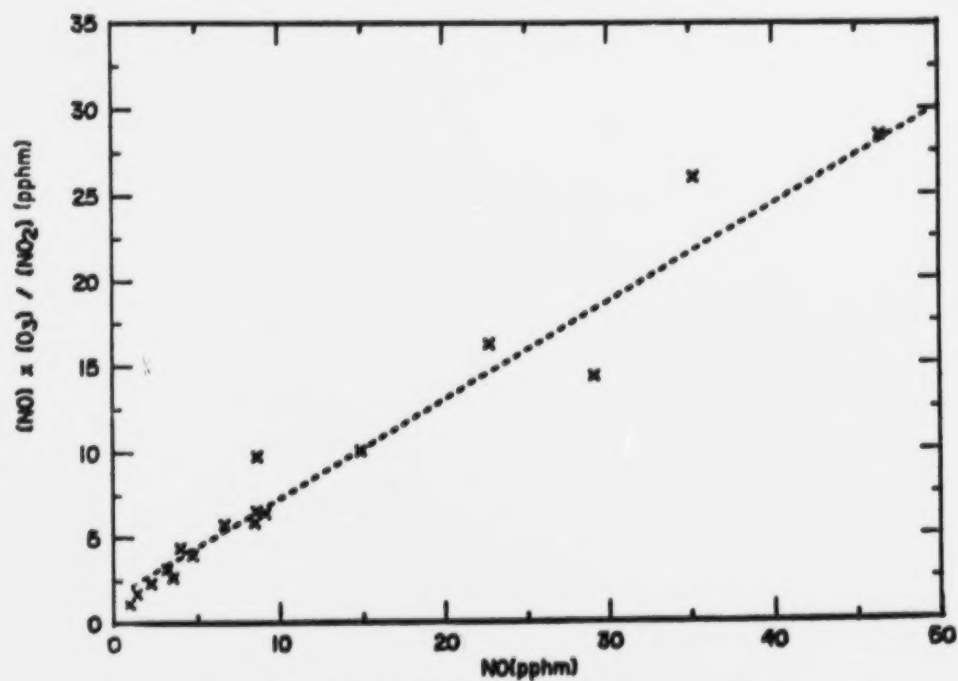


(b) 25 October 1972, 1138 to 1218 PST

FIGURE 25  $[NO] [O_3] / [NO_2]$  RATIOS VERSUS NO CONCENTRATION FOR TETROON RUNS (5-minute averages)



(c) 26 October 1972, 0907 to 0947 PST



(d) 2 November 1972, 1141 to 1316 PST

FIGURE 25 [NO] [O<sub>3</sub>] / [NO<sub>2</sub>] RATIOS VERSUS NO CONCENTRATION FOR TETROON RUNS (5-minute averages) (Concluded)

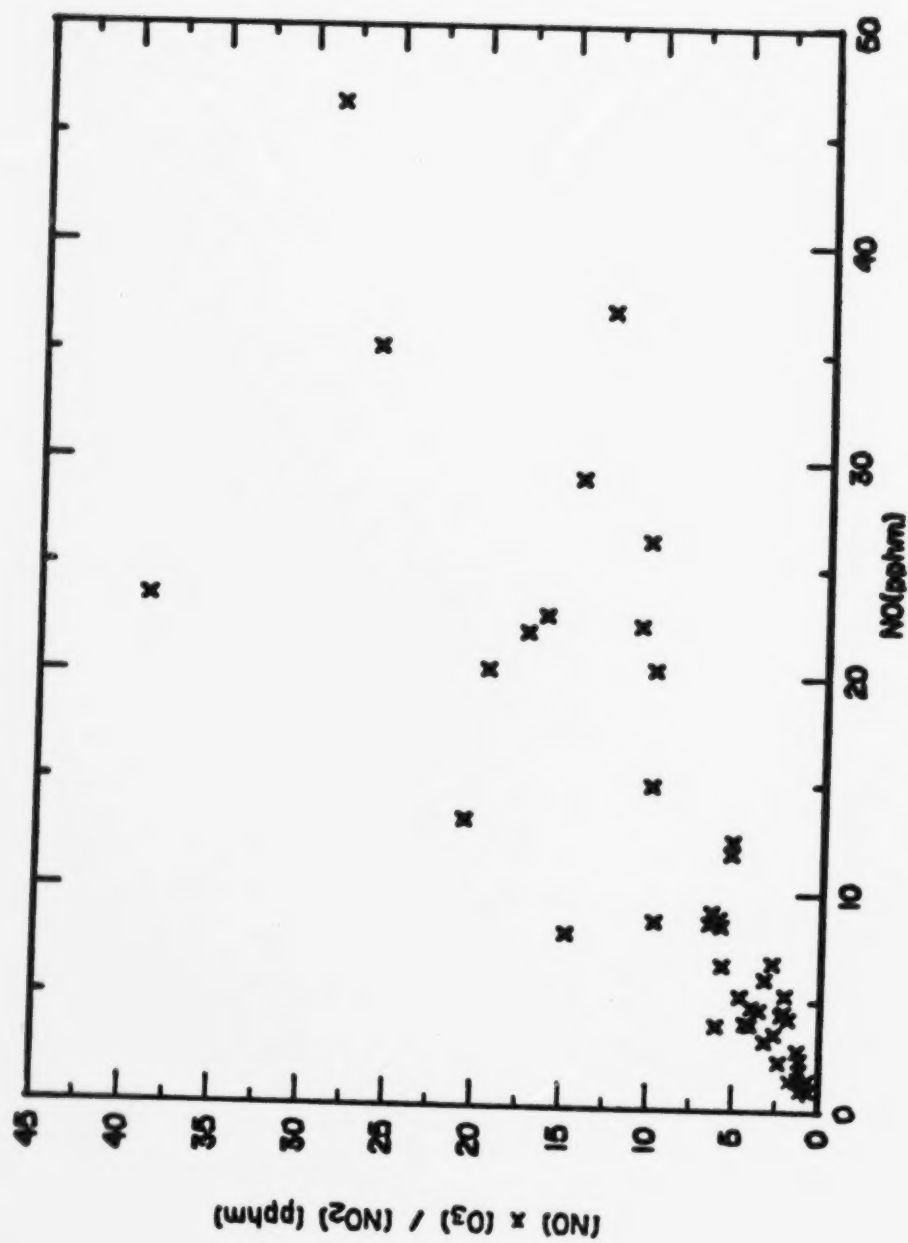


FIGURE 26  $[NO] [O_3] / [NO_2]$  RATIOS VERSUS NO CONCENTRATION, COMBINED DATA FROM FIGURE 25

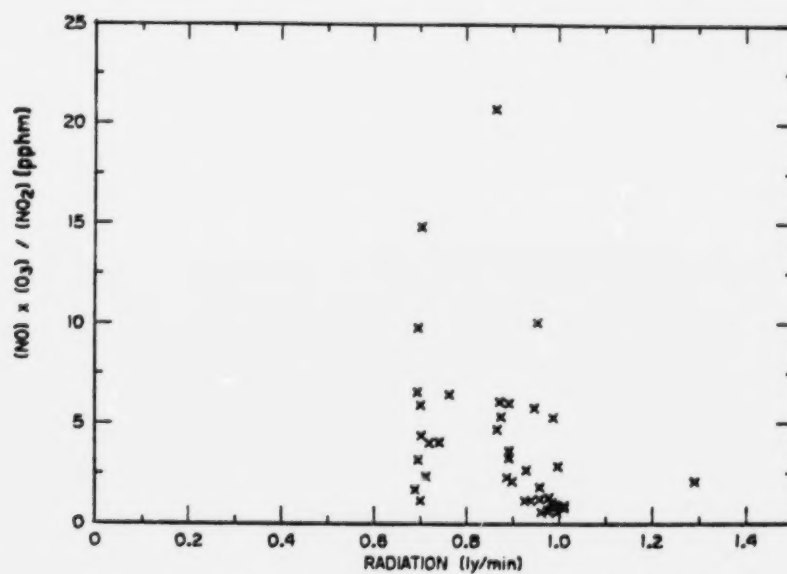
Table 8

## LINEAR LEAST-SQUARES FIT TO VALUES OF K

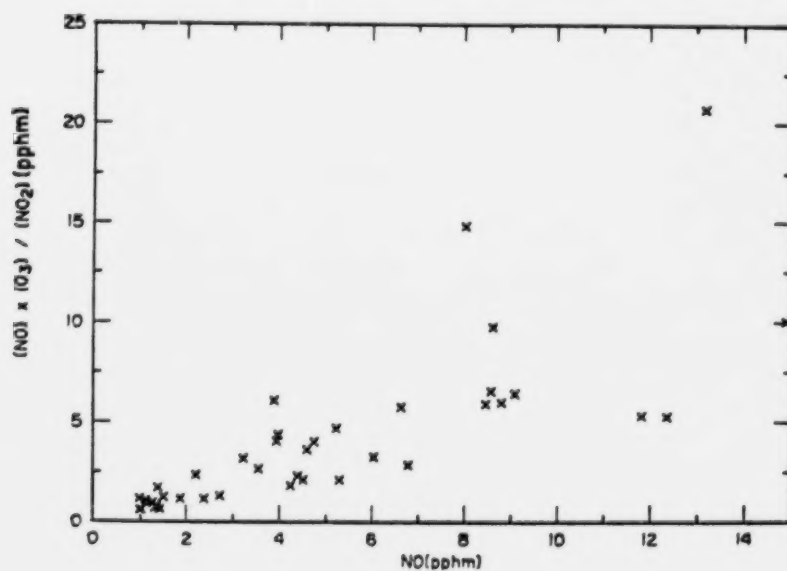
|                                     | <u>Slope</u> | <u>Correlation<br/>Coefficient</u> | <u>Photochemical<br/>Activity</u> |
|-------------------------------------|--------------|------------------------------------|-----------------------------------|
| Correlation with Solar<br>Intensity |              |                                    |                                   |
| 21 September                        | 45.5         | 0.37                               | High                              |
| 25 October                          | - 7.2        | -0.35                              | Low                               |
| 26 October                          | 4.0          | 0.027                              | Very low                          |
| 2 November                          | 57.4         | 0.68                               | Medium                            |
| Combined data                       | - 7.2        | -0.09                              |                                   |
| Correlation with NO                 |              |                                    |                                   |
| 21 September                        | 0.35         | 1.00                               | High                              |
| 25 October                          | 0.45         | 0.94                               | Low                               |
| 26 October                          | 0.48         | 0.67                               | Very low                          |
| 2 November                          | 0.63         | 0.97                               | Medium                            |
| Combined data                       | 0.58         | 0.87                               |                                   |

The correlation coefficients with NO are high in all cases. One reason for the high correlation with NO is that in cases where exhaust contamination is observed, the NO concentration will be high. Furthermore, the rate of reaction (11) is slow enough that equilibrium (14) will not be reestablished before the exhaust-containing air is sampled. In an attempt to eliminate the effects of exhaust contamination, all data for NO concentrations greater than 15 pphm were excluded, the data for the four days were replotted (Figure 27), and the correlation coefficients recalculated. For K versus radiation, the slope was -10.4 with a correlation of -0.33; for K versus NO concentration, the slope was 0.84 with a correlation of 0.77.

There are possible errors in the radiation measurement due to dirt or sea spray on the pyranometer or to variations caused by boat roll.



(a)  $[NO] [O_3] / [NO_2]$  Ratios Versus Solar Intensity



(b)  $[NO] [O_3] / [NO_2]$  Ratios Versus NO Concentration

FIGURE 27 COMBINED DATA FROM FIGURES 25 AND 26 WITH DATA FOR NO CONCENTRATION GREATER THAN 15 pphm OMITTED (5-minute averages)

These errors do not explain the wide variation that was observed in solar intensity. If the two high values of K are excluded in Figure 22(b), the value of K would be less dependent of the NO concentration. However, the correlation with light intensity is still not good.

A detailed comparison of the ratio calculated with smog chamber and atmospheric measurements from other studies with solar intensity is beyond the scope of this research program. We have evaluated some recent data reported by Demerjian, Kerr, and Calvert for chamber experiments and theoretical calculations of K.<sup>14</sup> In all cases, they used a value of  $k_a = 0.48 \text{ min}^{-1}$ , which corresponds to a solar zenith angle of 40 degrees. These data are given in Table 9. The average value of K is about 2.1 pphm from their theoretical data. However, experimental values from smog chambers are badly scattered, probably due to the poor accuracy of NO measurements at low concentrations. Since these data are calculated or measured at one level of solar intensity, it is difficult to compare the two types of measurements.

For future work, a more intensive analysis should be made of our data as well as the literature. A small modeling effort should be made to calculate values of  $k_a$  and K for other solar intensities. An ultraviolet sensor and an Eppley pyranometer should be added to the instrument complement. Data from an ultraviolet sensor would provide a better estimate of  $k_a$ .

Table 9

VALUES OF  $[\text{NO}][\text{O}_3]/[\text{NO}_2]$  FROM OTHER WORK<sup>14</sup>

| Initial Conditions<br>(pphm)                                            | Irradiation<br>Time<br>(min) | $[\text{NO}][\text{O}_3]/[\text{NO}_2]$<br>(pphm) |              |
|-------------------------------------------------------------------------|------------------------------|---------------------------------------------------|--------------|
|                                                                         |                              | Predicted                                         | Experimental |
| $[\text{NO}] = 7.5; [\text{NO}_2] = 2.5; [\text{HC}] = 0$               | 60                           | 2.1                                               | --           |
| $[\text{NO}] = 2.5; [\text{NO}_2] = 7.5; [\text{HC}] = 0$               | 60                           | 2.1                                               | --           |
| $[\text{NO}] = 90; [\text{NO}_2] = 10;$<br>$[\text{Propylene}] = 210$   | 25                           | 1.8                                               | 0.69         |
|                                                                         | 50                           | 1.9                                               | 1.8          |
|                                                                         | 75                           | 2.9                                               | 5.1          |
|                                                                         | 100                          | 2.3                                               | 6.3          |
| $[\text{NO}] = 7.5; [\text{NO}_2] = 2.5;$<br>$[\text{t-2-Butene}] = 10$ | 20                           | 1.8                                               | --           |
|                                                                         | 60                           | 2.0                                               | --           |

D. Observed Pollutant Inhomogeneity over San Francisco Bay

Apparent "pockets" of air containing high NO concentrations were frequently observed during tetron runs when new air was continuously overrun at the surface. These pockets were characterized by inhomogeneous NO concentrations (based on the variability in the data used to calculate the 5-minute averages), no corresponding increase THC, CO, and CN concentrations, and no corresponding decrease in O<sub>3</sub> concentration (due to reaction 11). Two explanations are possible; first, the NO was from shore sources, and second, it resulted from contamination by house-boat exhaust. The data do not adequately fit either explanation.

During intervals when exhaust gas contamination was known to occur, simultaneous increases in the concentrations of NO, CO, and CN were observed. Of these indicator pollutants, both NO and CN are extremely sensitive indicators of contamination, whereas CO is far less reliable

in identifying intervals of contamination. During maneuvers where the houseboat crossed its own path, increases in CN concentration were always observed but increases in NO concentrations may or may not be observed. Furthermore, the inlet to the sample mast was located 6 meters above and 7 meters forward of the exhaust gas exit ports of the houseboat. Since these "pockets" of air containing high NO concentrations were repeatedly observed when the houseboat was traveling at speeds greater than 20 km/hr, the source of NO cannot be satisfactorily explained by exhaust gas contamination.

Complex calculations of the turbulent mixing occurring in the wake of the houseboat underway at cruising speed have not been made and, realistically, probably could not provide accurate predictions of such mixing. The evaluation of the accuracy of such calculations could only be made by conducting experiments where exhaust gas constituents (NO, CO, and CN) are measured simultaneously from many locations on or near the houseboat superstructure. A definitive experiment of this nature was beyond the scope of this research project.

The PG&E power plants located at Hunters Point and Potrero Point (emissions of 15 tons of  $\text{NO}_x$  per day) could contribute to the observed inhomogeneities, but calculations of plume concentrations indicate that in most instances additional significant source contributions would be required to produce the NO concentrations observed. These power plants are the largest stationary source of  $\text{NO}_x$ , based on a list of pollutant sources supplied by the BAAPCD, that could significantly contribute to the burden within the area of interest. Other major stationary sources are located to the northeast near upper San Pablo and Suisun Bays. Due to the division of the wind flows, the emission from these other sources would not contribute to the atmospheric burden over the Bay near or to the south of San Francisco. The inhomogeneities of CN observed over the Bay are less significant since the sources of these particles are more

varied (combustion, sea spray, photochemical processes, and the like) and less well understood.

On the other hand, the observation that the  $O_3$  concentrations did not decrease in the presence of the high NO concentrations suggests that the source of NO is the houseboat exhaust. The half-life of reaction 11 is of the order of several seconds at the ambient concentrations. If the NO sources are on the shore, the time available for the NO to react with the  $O_3$  in the air parcel will be several minutes or longer. The observed  $O_3$  concentrations should be very low and certainly lower than those observed in the presence of the high NO concentrations. This anticipated reduction of the  $O_3$  concentration was not observed (with the exception of the data collected on 2 November near San Mateo Bridge, Figure 20). On the other hand, the residence time in the sampling line was 2 seconds which is short enough that only a small fraction of  $O_3$  should react.

The increase in the NO concentrations observed on specific occasions over San Francisco Bay without a corresponding increase in  $O_3$  concentration is compelling evidence suggesting partial exhaust gas contamination. The lack of substantiating increases in the concentration of CO and particularly CN during these intervals remains unexplained if contamination is actually the cause. The location of the sample inlet relative to the source of exhaust gases during traverses in the wind likewise nearly, but not absolutely, precludes exhaust gas contamination. The conflicting results obtained in this project cannot be interpreted with absolute certainty on the basis of known data.

## VII CONCLUSIONS AND RECOMMENDATIONS

### A. Applicability of Methods and Data for Model Verification

The objectives of this research project were twofold: first, determine the feasibility of a mobile laboratory to mark a parcel of air and measure the changes in constituents and concentration during aging; second, obtain measurements defining photochemical activity in tetraon-marked air parcels and present these in a form suitable for verification of photochemical models.

This research program demonstrated that a mobile laboratory can be used to follow an air parcel and to collect air quality data in a Lagrangian mode. Marking an air parcel by a tetraon is a feasible approach to a Lagrangian measurement of pollutant concentrations. Due to surface frictional effects, a wind shear of approximately  $-0.01$  m/sec/m was observed. This meant that the surface laboratory overran air parcels at a rate of about  $0.5$  m/sec. If the air parcel moves at speeds greater than about  $1.5$  m/sec, measurements can be made without contamination by the houseboat exhaust. At speeds of less than about  $1.5$  m/sec, the possibility of contamination is always present.

The appropriate logistics to effectively coordinate the operation of surface and airborne mobile laboratories were developed. The concept of using a houseboat as a mobile laboratory proved to be very effective. The houseboat provides a stable platform well suited for the operation of air quality instruments. The navigational procedures employed provided position fixes with excellent resolution throughout the Bay. The speed of the houseboat was adequate to accommodate tetraon tracking at a variety of wind speeds. The line power available from the onboard

generator had adequate stability for operation of the air quality sensors. The battery-inverter system was an adequate power supply for frequency-sensitive equipment such as the data tape recorder and the computer. The voltage decrease that was observed as the batteries discharged could be corrected by the use of a variable transformer.

The helicopter instrument package was designed to be easily installed and removed from a nondedicated helicopter. The procedures developed to keep the airborne instrument package warmed up and operational prior to installation in the helicopter were satisfactory. Communication between the house ~~and~~ and the helicopter was excellent. The equipment used and procedures developed during this research program represent a viable approach to the study of atmospheric photochemistry.

The measurement data obtained during the program, even though the pollutant concentrations were uniformly low, could provide useful data as to the role of photochemistry at low concentrations that approach the air quality standard and the concentration gradients that accompany these levels. In addition to pollutant measurements made during tetroon runs, a limited effort was made to map pollutant concentrations over San Francisco Bay and to identify the sources of emission responsible for the observed pollutants. During more normal meteorological conditions, wind flow patterns and wind speeds more conducive to photochemical smog formation would have been established. Under these conditions, the tetroon runs could more often have been initiated immediately downwind of an urban source with high concentrations of pollutant precursors to smog. In addition, the direction of tetroon travel under these conditions would have permitted longer tetroon runs and hence a longer interval for photochemical reactions to occur.

The observed microscale inhomogeneities in the distribution of pollutants over San Francisco Bay, particularly NO, were greater than anticipated. As discussed in the previous section of this report, two explanations are possible -- shore sources and exhaust gas contamination. The data do not adequately substantiate either explanation. Thus, on the basis of the data, the source of high NO concentration cannot be identified with absolute certainty.

The observations of pollutant concentrations immediately downwind of a large urban source also indicated that the pollutant burden was inhomogeneously mixed in the air mass. Wide variations in pollutant concentrations were observed both spatially and temporally downwind of San Francisco. At distances of less than 2 kilometers offshore of San Francisco, the urban source must be considered as a multiplicity of individual sources rather than a diffuse source. Thus, tetron runs with the objective of determining a mass balance should be initiated as a sufficient distance downwind of an urban source to ensure homogeneity through adequate mixing. The determination of a mass balance could also be accomplished by vertical and horizontal concentration mapping and averaging by the mobile laboratories prior to tetron launch. This technique coupled with simulation modeling to predict the pollutant contribution of adjacent air masses, through vertical and horizontal diffusion, could provide the basis for a mass balance determination in the air parcel under observation.

A major problem encountered under certain operational modes was contamination of the gas samples (and, to a lesser extent, the particulate samples) by engine exhaust. In addition to raising the height of the sample inlets, modifications to the engines could be made to reduce the exhaust emissions. Two alternative types of controls could be used: a combination of exhaust gas recirculation and a catalytic converter or modification of the induction system so that very lean operation is possible.

Catalytic converters would require complete overhaul of the engines and replacement of the exhaust systems to remove all traces of lead deposits. It would be necessary to use unleaded gasoline. Prototype induction systems have been shown (at SRI as well as elsewhere) to permit very lean operation (an air to fuel ratio of 18 or higher) at constant speed operation. This operational mode decreases hydrocarbon and  $\text{NO}_x$  emissions very effectively (factors of 10 or higher). The major problem is that satisfactory operation during acceleration or deceleration is not possible with current devices known to us. Since the houseboat was normally operated at a constant speed, one could release the tetroon and then adjust the air to fuel ratio to minimize the exhaust emissions.

In summary, the acquired data will be useful for photochemical modeling of low pollution conditions. The measurement approach was sound and a wealth of valid measurements were obtained. In addition, a good understanding was acquired of meteorological conditions over the Bay with respect to shore observations. The knowledge gained during this research program will provide an excellent basis for future photochemical studies over San Francisco Bay.

#### B. Recommendations for Future Research

A follow-on program is strongly recommended that would capitalize on the extensive experience SRI has gained in this program. It should begin in June to increase the likelihood that high smog levels could be studied. Although the basic approach used in this program was viable, several changes are recommended:

- Provide a better facility to weigh off tetroons--A transparent plexiglas housing should be fabricated and located on the deck space forward of the main cabin of the houseboat. This housing would provide a turbulence-free location to accurately weigh off tetroons during full or partial exposure to sunlight. Also, the transparent walls of the shelter would not blind the lower cabin, which was the case during intervals when the tetroon shelter was erected. Better tetroon weigh-off procedures are required so that the tetroons will float at lower altitudes.
- Locate sample inlet mast at a higher elevation--The sample inlet mast should be extended above the houseboat as high as is practical; it could easily be extended 11 meters or more above the water. The additional height would reduce the possibility of exhaust gas contamination and improve the ratio of sample inlet height to tetroon height. The higher sample mast in conjunction with tetroon flights at lower altitude would also improve the objective of measurement in a discrete air parcel.
- Mount a wind vane and anemometer--A permanently mounted recording wind vane and anemometer should be mast-mounted on the houseboat. These wind measurements should be integrated into the data acquisition system and recorded on the data tape. The compass heading at selected intervals could be entered manually into the data acquisition system by teletype. If a navigation compass with an analog output voltage could be obtained or fabricated, the inclusion of these measurements into the data would be very useful. The wind vane and anemometer would primarily serve to log differential wind speed and directions.
- Gimbal the solar intensity sensor--The solar intensity sensor should be replaced with an Eppley pyranometer mounted on a gimbaled platform to reduce short-term variation due to boat motion. A gimbaled ultraviolet sensor should be added to the instrument complement.
- Delete the gas chromatograph from the onboard instrumentation--The gas chromatograph did not operate in a satisfactory manner under the normal motions of the boat. Cryogenic samples should be collected at 1/4 to 1/2 hourly intervals and returned to the laboratory for analysis of selected samples.

- Install a catalytic accessory for THC sensor--A switchable catalytic converter should be installed in series with the inlet to the THC sensor to provide methane only and THC measurements. The catalytic converter would be operated at periodic intervals to obtain in-situ methane measurements.
- Delete the Lundgren impactor from the aerosol instrumentation--A two-stage collector for particulate material should be substituted for the Lundgren impactor. The design of the Lundgren does not permit sample foils to be easily installed or removed. The sample analysis is complex, expensive, and does not provide particulate data vital to understanding the photochemical processes.
- Increase the frequency of particulate collection--The high-volume samples collected during this measurement program were large enough that shorter collection times of 1 hour or less should be used. This data would permit a more accurate determination of the mass balance.
- Shock-mount the nondispersive infrared CO analyzer--The NDIR CO analyzer should be shock mounted to improve the signal-to-noise ratio at cruising speeds. At tetroon tracking speeds, the performance of the NDIR was adequate without shock mounting.
- Use a different measurement principle for airborne CO measurements--The mercury displacement CO analyzer used in the helicopter was not satisfactory. Concentration gradients or relative measurements could be made, but absolute concentrations were difficult to retrieve from the acquired data. An Andros Isotope Fluorescence CO analyzer is recommended for future airborne instrumentation.
- Improve communication and in situ recording of conversation and radio transmissions--The houseboat should be equipped with an intercom system with voice recording of all communication between the bridge and the main cabin. In addition, communication from the houseboat to the helicopter should be directly to the instrument operator rather than relayed through the pilot.
- Improve instrumentation for wet and dry bulb temperatures--The wet bulb temperature measurement was erratic due to the design of the wick reservoir.

- Reduce houseboat engine emissions--Equip the houseboat engines with an induction system designed to reduce HC and NO<sub>x</sub> emissions through the use of a very lean air to fuel mixture.

These recommendations do not represent basic changes in the approach that was employed during this research program. However, they do represent changes in equipment or operating techniques that, if incorporated, would improve data capture and data interpretation for future studies.